STUDIES ON PHASE FORMATION IN HIGH ALUMINA CEMENT BY VARYING MANUFACTURING PARAMETER AND EFFECT OF THOSE PHASES IN REFRACTORY CASTABLE

A

THESIS SUBMITTED IN PARTIAL FULFILLMENT

OF THE REQUIREMENT FOR THE DEGREE OF

Master of Technology

in

Ceramic Engineering

By
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Department of Ceramic Engineering
National Institute of Technology
Rourkela

2011-2013

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CERTIFICATE

This is to certify that the thesis entitled, **"STUDIES ON PHASE FORMATION IN HIGH ALUMINA CEMENT BY VARYING MANUFACTURING PARAMETER AND EFFECT OF THOSE PHASES IN REFRACTORY CASTABLE"** submitted by **Mr. Aditya Prakash Shrimali** in partial fulfillments of the requirements for the award of **Master of Technology** degree in **Ceramic Engineering** at **National Institute of Technology**, **Rourkela** is an authentic work carried out by him under our supervision and guidance.

To the best of our knowledge, the matter embodied in the thesis has not been submitted to any other University/ Institute for the award of any Degree or Diploma.

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Acknowledgement

It is with a feeling of great pleasure that I would like to express my most sincere heartfelt gratitude to **Prof. S. Bhattacharyya**, Dept. of Ceramic Engineering, NIT, Rourkela for suggesting the topic for my thesis report and for his ready and noble guidance throughout the course of my preparing the report. I thank you Madam for your help, inspiration and blessings.

I would like to express my heartfelt thanks and deep sense of gratitude to my honorable research supervisor **Mr. B Prasad**, GM (R&D), Concast, Castable & Precast, OCL India Limited, Rajgangpur for his constant encouragement, efficient planning and valuable guidance during the entire course of my work.

I express my sincere thanks to **Prof. S. K. Pratihar**, Head of the Department of Ceramic Engineering, NIT, Rourkela for giving me the opportunity to go to OCL India Limited, Rajgangpur carrying my project and providing me the necessary facilities in the department.

I also express my thanks to **Sk. Bashir Mohammed**, General Manager, Castable & Precast, OCL India Limited, Rajgangpur for providing me the necessary facilities in the department. I would also express special thanks to **Mousam Bag**, Production Superintend Castable Department for his constant encouragement and guidance. I would also wish to express my gratitude and sincere thanks to my honorable teachers **Prof. S. Bhattacharyya, Prof. J. Bera, Prof. B. B. Nayak**, **Prof. S. K. Pal**, **Prof. R. Majumder, Prof. S. Dasgupta** and **Prof. A. Choudhury** for their invaluable advice, constant help, encouragement, inspiration and blessings.

Submitting this thesis would not be possible without the constant help, encouragement, support and suggestions from Ph.D Scholars and friends of my Department. I am very much thankful to them for their time to help.

Last but not least I would like to express my gratitude to my parents and other family members, whose love and encouragement have supported me throughout my education. I would also express my sincere thanks to laboratory Members of Department of Ceramic Engineering, NIT, Rourkela and Research & Development Department, OCL India Limited, Rajgangpur for constant practical assistance and help whenever required.

Contents

Certificate
Acknowledgement
List of Figure and Tables
Abbreviations Used
Abstract

Chapter-1 Introduction & Objective **2-9**

1.1. Introduction
1.2. Objective **3**

Chapter-2 Literature Reviews **10-25**

2.1. Raw Materials **11**
2.1.1. Calcareous material **11**
2.1.2. Aluminous Materials **11**
2.2. Production of High Alumina Cement **12**
2.3. Calcium Aluminate Phases present in CACs **13**
2.4. Preparation of CACs by Varying Various Parameters **15**
2.5. Synthesis of Calcium Aluminate Phases by Different Route **17**
2.6. Additives for HAC Products **20**
2.7. Hydration of HAC's **21**
2.8. Dehydration of HAC's **23**

Chapter-3 Experimental Procedure **26-35**

3.1. Materials & Compositions **27**
3.1.1. Stage-1 Preparation of HAC's **29**
3.1.2. Batch Preparation **29**
3.1.3. Nodules Formation **29**
3.1.4. Drying **29**
3.1.5. Sintering **29**
3.1.6. Clinker Cooling & Grinding **29**
3.2. Stage-2 Castable formation using self-prepared cements **31**
3.2.1. Batching **31**

3.2.2. Mixing **31**
3.2.3. Casting **31**
3.2.4. Drying **33**
3.2.5. Firing **33**
3.3. Evaluation of properties **33**
3.3.1. Determination of AP and BD of the Castable **33**
3.3.2. Cold Crushing Strength (CCS) **34**
3.3.3. Cold Modulus of Rupture (CMOR) **34**
3.3.4. Phase Identification (X-RD) **35**

Chapter-4 Result & Discussion **36-59**

4.1. Results & Discussion **37**
4.2. Characterization Self-prepared HACs **37**
4.2.1. Chemical Analysis of Cement **37**
4.2.2. Mineralogical or XRD (Quantitative) Analysis **38**
4.3. Characterization of castable group D **48**
4.3.1. Chemical Analysis **48**
4.3.2. Mechanical Properties **48**
4.4. Characterization of castable group E **51**
4.4.1. Chemical Analysis **51**
4.4.2. Mechanical Properties **51**
4.5. Characterization of castable group F **54**
4.5.1. Chemical Analysis **51**
4.5.2. Mechanical Properties **51**
4.6. Comparison of Mechanical Properties **57**

Chapter 5 Conclusion **60-61**

Chapter 6 References **62-66**

List of Figures and Tables

Fig. 1.1. $CaO-Al_2O_3$ Binary Phase Diagram

Fig. 2.1. Schematic representation of temperature profile in arbitrary units (a.u.) as a function of time for a CAC suspension.

Fig. 2.2 The hydration/dehydration process

Fig. 3.1. Flow Chart for preparation of HAC (Lab Scale)

Fig. 3.2. Flow chart for preparation procedure of castable

Fig.4.1 XRD analysis of Cement A fired at 1430^oC

Fig.4.2 XRD analysis of Cement A fired at 1470^oC

Fig.4.3 XRD analysis of Cement B fired at 1430^oC

Fig.4.4 XRD analysis of Cement B fired at 1470^oC

Fig.4.5 XRD analysis of Cement C fired at 1430^oC

Fig.4.6 XRD analysis of Cement C fired at 1470^oC

Fig.4.7 XRD analysis of Cement D fired at 1430^oC

Fig.4.8 XRD analysis of Cement D fired at 1470^oC

Fig.4.9 XRD analysis of Cement E fired at 1430^oC

Fig.4.10 XRD analysis of Cement E fired at 1730^oC

Fig.4.11 XRD analysis of Cement F fired at 1430^oC

Fig.4.12 XRD analysis of Cement F fired at 1470^oC

Fig. 4.13 Variation CA phase with varying Composition

Fig. 4.14 Variation CA_2 phase with varying Composition

Fig. 4.15 Different Phases in Different self-prepared HACs

Fig. 4.16 Variation in CCS for Castable Group D

Fig. 4.17 Variation in CMOR for Castable Group D

Fig. 4.18 Variation in CCS for Castable Group E

Fig. 4.19 Variation in CMOR for Castable Group E

Fig. 4.20 Variation in CCS for Castable Group F
Fig. 4.21 Variation in CMOR for Castable Group F
Fig 4.22 Variation in CCS of castables prepared by cements fired at 1430^{o}C
Fig 4.23 Variation in CCS of castables prepared by cements fired at 1470^{o}C
Fig 4.24 Variation in CMOR of castables prepared by cements fired at 1430^{o}C
Fig 4.25 Variation in CMOR of castables prepared by cements fired at 1470^{o}C

List of Tables

Table 1.1 ASTM classification of Refractory Castable
Table 1.2. Classes of calcium aluminate cements on the basis of purity
Table 1.3. Properties of CAC Mineral Constituents
Table 1.4. Typical mineral constituents of calcium aluminate cements
Table 3.1. Chemical Analysis of Raw Materials used
Table 3.2. Composition of Different High Alumina Cements (HAC's) prepared
Table 3.3. Composition of Castable
Table 4.1 The Chemical Analysis Result of All The Self-Prepared Cements
Table 4.2 Percentages of Different Phases in All Self-Prepared Cements
Table 4.3 Chemical Composition of Castable Group D
Table 4.4. Mechanical Properties of Castable Group D
Table 4.5 Chemical Composition of Castable Group E
Table 4.6. Mechanical Properties of Castable Group E
Table 4.7 Chemical Composition of Castable Group F
Table 4.8. Mechanical Properties of Castable Group F

Abbreviations Used

ASTM	America Standard for Testing and Materials
^{o}C	degree Celsius
cm	centimeter
Kg	Kilogram
gm	gram
min	minute
C	lime (CaO)
A	Alumina (Al_2O_3)
S	Silica (SiO_2)
CAS	Anorthite
C_2AS	Gehlenite
CA	Monocalcium aluminate
CA_2	Calcium di-aluminate (Grossite)
$C_{12}A_7$	Dodeca-calcium hepta aluminate (Maynite)
CA_6	Calcium hepta aluminate (Hibonite)
AH_3	Gibbsite
HAC	High Alumina Cement
AP	Apparent Porosity
BD	Bulk Density
CCS	Cold Crushing Strength
CMOR	Cold Modulus of Rupture
Wt.%	Weight percent
µ or µm	Micrometer

Abstract

Unshaped refractories are superior over shaped refractories with respect of ease installation, durability, safety, cheaper, joint less or minimum joint structure and so on. In unshaped refractories, High- alumina cements (HACs) are the main binder and are currently most in demand. In the first generation of unshaped refractory the HACs were the one and only binding agent used. The good corrosion resistance and refractory properties of HAC account for its wide use in refractory concretes.

The major mineral phases present in HACs are Monocalcium aluminate (CA), Monocalcium dialuminate (CA_2), Dodecacalcium heptaaluminate ($C_{12}A_7$) and α-Al_2O_3. Depending on the prescribed setting times and mechanical properties of unshaped refractories in accordance with their application area, the quality or desired characteristics of HACs changes. All the properties of HACs depend only on its mineralogical phase composition. Just as CA phase is responsible for development of highest strength among all other Calcium Aluminate phases and relatively reduces the time during hydration. So for the achievement of desired characteristics or properties of the refractory or HACs the major concern must be taken in its phase composition.

So in the present work attempt has been made to prepare HACs by varying operating parameter such as starting composition, raw materials and sintering temperature (during manufacturing) and study the effect of mineralogical composition of those cements on the properties of final product (refractory castable). In the preparation of HACs, alumina content and alumina sources (partially) were varied and sintering was done at two different temperatures 1430^{o}C and 1470^{o}C. Prepared HACs were characterized chemically & mineralogically (Phase Analysis). Castables were made by using those HACs and were characterized chemically and mechanically.

Chapter-1

Introduction & Objective

1.1 Introduction:-

Refractories are non-metallic materials that are hard to melt at high temperatures with enough mechanical strength and heat resistance to withstand rapid temperature changes, including repeated heating and cooling. They have also good corrosion and erosion resistance to molten metal, glass, slag, and hot gases etc. The ASTM C71 defines the refractories as "nonmetallic materials having those chemical and physical properties that make them applicable for structures or as components of systems that are exposed to environments above 1000^0C". [1] Refractories can be classified in two ways, first is physical classification, on the basis of different product forms & another is chemical classification on the basis of different chemical compositions. Under physical classification refractories are classified in three types, namely; shaped refractories, unshaped refractories and fibrous materials (ceramic fiber). Unshaped refractories are further classified in many types accordingly their preparation and installation method. One of most common & important out of them is "castable refractories".

During World War II in the USA, as a substitute for special brick shapes used in boilers & oil refineries, castables were developed. Because of many advantages of them over shaped refractories, castables began to produce after World War. Castables are made from refractory aggregates and bonding agents. [2]

The ASTM C401-91, Standard Classification of Alumina and Alumina Silicate Castable Refractories, the following classification exists based upon chemistry and lime content. A proper classification should include as much information as possible about the chemical nature, rheological behavior, and installation characteristics of the castable. [41,42]

Table 1.1 ASTM classification of Refractory Castable

CASTABLE CLASSIFICATION	LIME CONTENT
Regular Castable Refractory	CaO > 2.5%
Low Cement Castable Refractory	1.0% < CaO < 2.5%
Ultra-Low Cement Castable Refractory	CaO < 1.0%
No Cement Castable Refractory	CaO < 0.2%

In the first generation of unshaped refractory the High-alumina cements were the one and only binding agent used. Their properties include development of high strength within 6 to 24hr of placement, good corrosion resistance, good resistance to sulfates and refractory properties. [3]

Such properties of HACs account for its wide use in refractory concretes. Mostly all properly cured castables require only 24hr to develop 70-80% full strength.

Until the early 1950s, commercially available HAC contained large amounts of Fe_2O_3 & SiO_2 as impurities. The presence of these oxides limited the use to relatively low-temperature applications. In late1950s, higher purity calcium aluminate cements were came into light which expanded the use of refractory castables to higher temperature applications. The recent classification of HAC's comprises only three groups on the basis of alumina content and purity; low purity, intermediate purity and high purity and given in Table 1.1. Higher purity CAC's were introduced during the 1950s which expanded the use of refractory castables to include higher temperature applications. [4]

Table 1.2. Classes of calcium aluminate cements on the basis of purity

Type	**Low Purity**	**Intermediate Purity**	**High Purity**
Composition Range wt%			
SiO_2	4.5-9.0	3.5-6.0	0.0-0.3
Al_2O_3	39-50	55-66	70-90
Fe_2O_3	7-16	1-3	0-0.04
CaO	35-42	26-36	9-28

Lime stone or simply lime with bauxite or other aluminous material low in silica (SiO_2) are mainly used to made CAC's. CAC's are formed by reaction of lime and alumina either by a sintering or clinker process or from fusion. More appropriately "Calcium aluminate cements are obtained by fusing or sintering a mixture of suitable proportions of aluminous and calcareous materials and grinding the resultant product to fine powder". [5]

The predominant method of manufacture of HAC is by sinter clinker process. With the new development and desired properties of CAC's the manufacturing process changed very much. Now days, raw mix of proportioned hydrated lime or limestone and calcined alumina is either fed as-ground or as agglomerate (may be in nodules, granules & briquette form) into a rotary kiln, similar to that used in the manufacture of Portland cement. The product is sintered at 1450-1500^oC, cooled and then ground to cement fineness together with any additives. These include Calcined alumina to obtain the desired Al_2O_3 content, gypsum or other materials to control the set. On sintering the raw mix generally transforms into higher alumina phases as the material temperature increases inside the kiln. [4, 5]

Both CaO/Al_2O_3 ratio and temperature determine the amount and type of calcium aluminate phases formed during the process. In $CaO\text{-}Al_2O_3$ binary phase diagram (Figure 1), five binary phases are identified, namely C_3A, $C_{12}A_7$, CA, CA_2 & CA_6. Liquidus temperatures drop rapidly, upon addition of Al_2O_3 to CaO. C_3A melts incongruently to CaO & liquid, at 1535°C. Minimum melting compositions are the eutectics between $C_{12}A_7$ & either C_3A or CA and are located at 1400°C & 1395°C. With the increasing alumina amount, liquidus temperatures begin to increase rapidly. At 1608°C, CA melts incongruently to CA_2; at ~1790°C, CA_2 melts incongruently to CA_6. CA_6 melts incongruently at~1860°C to Al_2O_3 and liquid. CACs having CaO/Al_2O_3 ratios between 0.9 and 1.2 have lower solidus & liquidus temperatures than which have CaO/Al_2O_3 ratios between 1.8 and 2.5. If their CaO/Al_2O_3 ratio is less than 1.0, $C_{12}A_7$ & CA phases are expected to contain as principal phases CACs. High alumina cements, depending on their CaO/Al_2O_3 ratio, contain mainly CA & CA_2, or with increasing Al_2O_3 content, CA_2 & CA_6. [6, 7, 8]

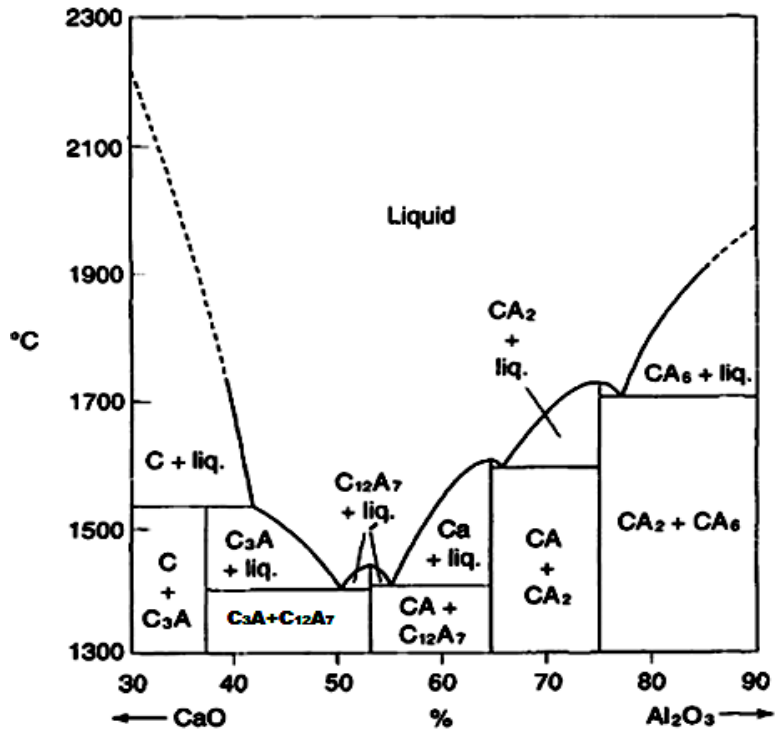


Figure 1.1. $CaO\text{-}Al_2O_3$ Binary Phase Diagram

The formation of calcium aluminate in clinker takes place in accordance with the scheme-

$$C+A \longrightarrow C_3A + A \longrightarrow C_{12}A_7 + A \longrightarrow CA + A \longrightarrow CA_2 + A \longrightarrow CA_6$$

High purity CAC sinters readily, even though very refractory high purity lime stone and calcined alumina are used as starting raw materials. At approximately 50wt% CaO/Al_2O_3, a eutectic occurring at 1360^oC enhances liquid phase sintering of these refractory oxides. [3]

The most critical areas of cement production are development of the clinker phases and the grinding process. Not only the amount and proportions of clinker phases are important but also their reactivity. With a decrease in C/A ratio, activity of calcium aluminates with respect to hydration is known to decrease. Control of the particle size on grinding is important, because variations in the particle size distribution can not only affect cement hydration, but also its reactivity with the aggregates in the concrete.

The ultimate properties of the castables like workability, hardening and also the placing properties have major impact by the mineralogical composition of the calcium aluminate cements. The Monocalcium Aluminate (CA or $CaO.Al_2O_3$) is the principal hydraulic phase present in calcium aluminate cements. It accounts around ~40% of the total mineralogical composition of calcium aluminate cements.

The CA_2 phase also appears in addition to other phases like CA and $C_{12}A_7$ with the increasing aluminous content in the calcium aluminate cement and sometime also α-Al_2O_3 develops after sintering. But the C_3A and CA_6 phases are not normal or desired constituents of the calcium aluminate cement but CA_6 appears very rarely. The presence of silica and iron oxide (ferric or ferrous) always results in very complex phase equilibrium assemblages which always include CA & ferrite solid solution (Fss). [3, 5, 9]

When they are mixed with water, the hydraulic minerals begin to dissolve quickly forming a saturated solution of ions. In CAC's Ca^{+2} and $Al(OH)_4$ ions form. Nucleation and crystal growth of hydration products produces an interlocked network that gives setting and then develops strength. Rates of hydration are dependent of the starting CaO/Al_2O_3 ratio and temperature. With a decrease in C/A ratio, activity of calcium aluminates with respect to hydration is known to decrease. [44]

Table 1.3. Properties of CAC Mineral Constituents [14]

Mineral	Chemical composition (wt. %)				Tm (^oC)	Density g/cm^3	Crystal system
	CaO	Al_2O_3	Fe_2O_3	SiO_2			
C	99.8	-	-	-	2570	3.32	Cubic
$C_{12}A_7$	48.6	51.4	-	-	1405-1495	2.69	Cubic
CA	35.4	64.6	-	-	1600	2.98	Mon.
CA_2	21.7	78.3	-	-	1750-1765	2.91	Mon.
C_2S	65.1	-	-	34.9	2066	3.27	Mon.
C_4AF	46.2	20.9	32.9	-	1415	3.77	Orth.
C_2AS	40.9	37.2	-	21.9	1590	3.04	Tet.
CA_6	8.4	91.6	-	-	1830	3.38	Hex.
α-Al_2O_3	-	99.8	-	-	2051	3.98	Rhombo.

The hydration of CA occurs through initial dissolution and subsequent precipitation of CAH_{10} and C_2AH_8 from the super saturated solution. Before precipitation an induction period occurs.

$$CA + 10H \rightarrow CAH10 \quad ...1$$

$$2CA + 11H \rightarrow C2AH8 + AH3 \quad ...2$$

$$3CA + 12H \rightarrow C3AH6 + 2AH3 \quad ...3$$

$$2CAH10 \rightarrow C2AH8 + AH3 + 9H \quad ...4$$

$$3C2AH8 \rightarrow 2C3AH6 + AH3 + 9H \quad ...5$$

Above all equations 1 to 5 shows the possible reactions during the hydration of CA. At temperatures below 10^oC, for CA, formation of CAH_{10} (eqn. 1) predominates, this phase continues to form up to about 27^oC. Between 10^oC to 27^oC CAH_{10} and C_2AH_8 are formed together (eqn 1&2). CAH_{10} no longer forms at higher temperatures and the stable phase C_3AH_6 occurs early in the hydration process. The formation of C_3AH_6 is always preceded by the transitory formation of some C_2AH_8, even at temperatures up to 90^oC, but the direct formation of C_3AH_6 from CA (eqn 3) can take place after some C_3AH_6 has been nucleated.
This phase rapidly becomes the only hydrate present when hydration occurs at temperatures above 50^oC. Eqn 4&5 show the conversion of the metastable hydrates. The rate of reactions

is dependent on temperature, moisture state and possibly other variables such as the water/cement ratio. The crystallization of AH_3 gel to gibbsite is also highly temperature dependent and sluggish at ambient temperatures. [10, 11, 12, 13]

Table 1.4. Typical mineral constituents of calcium aluminate cements [4]

Relative Hydration Rate	**Cement Purity**		
	Low	**Intermediate**	**High**
Fast	$C_{12}A_7$	$C_{12}A_7$	$C_{12}A_7$
Moderate	CA	CA	CA
Slow	CA_2 C_2S C_4AF	CA_2 C_2S C_4AF	CA_2
Nonhydrating	C_2AS CT A	C_2AS CT A	CA_6 A

During the heating, the bond phase undergoes various transformations. After casting & during drying or heating at 110^{o}C, the incomplete hydration continues to completion; crystallized gibbsite phase appears.

AH_3 & C_3AH_6 gradually decomposes to amorphous anhydrous and water vapor at or in between 100-400^{o}C. Porosity increases and strength decreases. In temperature range between 400-900^{o}C, subsequent dehydration of stable hydrates C_3AH_6 dehydrates to $C_{12}A_7$ & gibbsite transforms to alumina hydrate. Porosity continues to increase and strength also to decrease. In region between 800-1100^{o}C, porosity max & strength tends to minima, bonding phase first re-crystallize to $C_{12}A_7$ then CA from 950^{o}C onwards CA_2 formation begins. At about 1100^{o}C CA_2 reaches maximum. In case of 80% Al2O3 HAC's above 1300^{o}C CA_6 form from CA2 and Al_2O_3. Above 900^{o}C, CA crystallized and sintering began to occur and this led to ceramic bonding and improves strengths. [14]

1.2 Objective:-

In ultra-low cement castable formulation though the high alumina cement content is very low but still it plays an important role, particularly the phase composition of high alumina cement affect the strength development behavior of refractory concrete and castables made from them. In this work an attempt has been made to-

- Study the phase variation in High Alumina Cement with varying composition.
- Study the phase variation in High Alumina Cement with varying or replacing starting raw material.
- Study the phase variation in High Alumina Cement with varying firing temperature.
- To study the effect of those High Alumina Cement's on the properties of refractory castables.

Chapter-2

Literature Reviews

2.1 Raw Materials

2.1.1 Calcareous material

Calcium aluminate cements are prepared by mixing, fusion or firing & subsequent cooling and grinding of mixture of calcareous and aluminous materials. [4] Lime is used mostly. In the present work only hydrated lime was used because of its easy availability & purity factors. It is calcium hydroxide with the chemical formula of $Ca(OH)_2$. Hydrated lime, sufficient amount of water has already been added at the manufacturing stage to hydrate it completely.

2.1.2 Aluminous Materials

Different types of aluminous materials are used in various application areas under refractories. For the production of CACs many types of Al_2O_3 containing materials are used on the basis of quality or purity, requirement of end product and cost. For the production of high purity CACs calcined alumina is used. In the present work White fused alumina and reactive alumina were also used and replaced certain amount of calcined alumina in the composition. Calcined alumina offers plasticity, better rheological properties & plays a significant role in the flowability. [4] Calcined alumina is aluminum oxide that has been heated at temperatures in excess of 1,050°C to drive off nearly all chemically combined water. In this form, alumina has great chemical purity, high density, and a high melting point (slightly above 2,050°C). White fused alumina is produced by melting of calcined alumina at above 2040^oC in an electric arc furnace. It has very high chemical purity (>99% Al_2O_3), high refractoriness, abrasion resistance as well as chemical inert, but very expansive. "Reactive" alumina is the terms normally given to a relatively high purity and small crystal size (<1 mm) alumina which sinters to a fully dense body at lower temperatures than low soda, medium-soda or ordinary-soda aluminas. "Reactive" alumina powders are normally supplied after intensive ball-milling which breaks up the agglomerates produced after calcination. They are utilized where exceptional strength, wear resistance, temperature resistance, surface finish or chemical inertness are required. Again cost is the major factor. [20,21]

2.2 Production of High Alumina Cement

I. N. Sorokin et al. [22] produced high alumina cement by fusing a mixture of technical alumina with lime in electric arc furnace. Melting was carried out in an electric arc furnace at 1800^{o}C, the melt was then cast into balls or clinkers and after cooling it was crushed and ground to desired fineness of 4000-5000 cm^{2}/g. The major hydraulic active phases present were CA, CA_2 & $C_{12}A_7$ and inert one was CA_6.They showed that the high-alumina cement obtained by fusing a lime-alumina mixture has better characteristics.

O. V. Kvyatkovskii et al. [23] prepared high alumina cement by burning of granules and briquettes clinker in rotary kiln. The main advantages of rotary kilns are the possibility of mechanization and ensuring uniform calcination of the cement clinker. The milled alumina &lime mixture was moistened and then pressed to briquette (by using roller press with a tooth-rachet bandage attachment) and granules (by using Plate Granular) form. The prepared briquette or granules then were fired in rotary kiln at 1450-1500^{o}C and then cooled, crushed and finely ground. The predominant phase was CA_2 and other was CA in the prepared high alumina cement. They also calculated the dust removal during firing in both cases and showed that levels of dust removal were 4% for briquetted process whereas for granulated mixtures it was 33%.

In the USPTO patent no- US4204878A [24] the basic objective of the author is to provide the composition or raw mixture for the production high alumina cement. In this invention the raw mixture consists of a calcareous component, an aluminous component and a chloride of at least one of the metals selected from the group consisting of magnesium, calcium, barium, strontium, sodium and potassium. The object of addition of the chloride additive is based on the fact that these additives intensify the clinker formation process. The presence of these ensures formation of the liquid phase at a temperature within the range from 700 to 900^{o}C.

The principal object of this invention [25] was to provide a method of manufacturing high alumina cement which method is economical and having high early strength with desired slow set and to produce high alumina cement having improved thixotropic properties. Calcium carbonate of whiting grade was used as the calcareous component and high grade powdered alumina commercially known as Alcoa-14 and in another South American bauxite were used as aluminous component. Firing was performed in a rotary kiln, kiln length of 30

feet, an internal diameter of 21 inches, and a slope of 0.45 inch per foot, wherein the rotation is 1 revolution per minute and the feed rate such as to cause 5lbs per minute to be discharged.

The high alumina cement prepared by this method according to the invention are more thixotropic than previously known cements, high early strengths and the setting time was adjusted by fineness of the burned material discharged from the kiln.

2.3 Calcium Aluminate Phases present in CACs:-

The ultimate properties of the castables like workability, hardening and also the placing properties have major impact by the mineralogical or phase composition of the calcium aluminate cements. The Monocalcium Aluminate (CA or $CaO.Al_2O_3$) is the principal hydraulic phase present in calcium aluminate cements. It accounts around ~40% of the total mineralogical composition of calcium aluminate cement. The calcium aluminate cement lies in the two component system $CaO-Al_2O_3$, and must contain very less in iron oxide, silica & other minor components.

With the increasing aluminous content in the calcium aluminate cement the CA_2 phase also appears in addition to other phases like CA and $C_{12}A_7$ and sometime also $\alpha-Al_2O_3$ develops after sintering. But the C_3A and CA_6 phases are not normal constituent of the calcium aluminate cement CA_6 appears very rarely. The presence of silica and iron oxide (ferric or ferrous) always results in very complex phase equilibrium assemblages which always include CA & ferrite solid solution (Fss). And these are-

- CA-Fss-$C_{12}A_7$-FeO- Pleochroite
- CA-Fss-$C_{12}A_7$-C2S- Pleochroite
- CA-Fss -C2S-C_2AS - Pleochroite
- CA-Fss-C_2S-FeO- Pleochroite
- CA-Fss-C_2AS-FeO- Pleochroite

C_2S, C_2AS (Gehlenite) or both phases are the resultant phases if silica is present in CACs. The presence of silica should be very less otherwise it get reacted with alumina and produces less reactive phase C_2AS rather than reactive phase CA. The presence of iron oxide results in ferrite solid solutions in the series C_6AF-C_2F with substantial presence of SiO_2, TiO_2 and MgO. The existence of iron oxide results to formation of one or a combination of a spinel

phase, wustite (FeO) and Pleochroite. The presence of Pleochroite leads to strength deterioration and diminishes the CA content.

A) Monocalcium Aluminate (CA Or $CaO.Al_2O_3$)
B) Dodecacalcium Heptaaluminate ($C_{12}A_7$ Or $12CaO.7Al_2O_3$)
C) Monocalcium Dialuminate (CA_2 Or $CaO.2Al_2O_3$)
D) Monocalcium Hexaluminate (CA_6 Or $CaO.6Al_2O_3$)
E) Gehlenite (C_2AS)
F) Ferrite Solid Solution Or Tetra Calcium Alumino Ferrite (C_4AF)

A) Monocalcium Aluminate (CA Or $CaO.Al_2O_3$):-

CA is the most important phase and principal hydraulic compound present in the calcium aluminate cements. It accounts large percentage of total phase composition. It generally occurs in 40-70% and this phase has high melting point and it melts congruently at 1600oC. CA phase is responsible for development of highest strength among all other Calcium Aluminate phases and in relatively shortest time during hydration. Initially it takes time to set but once initial set reached it rapidly hardens. CA in CACs is a solid solution with higher refractive index than the pure compound, and its structure is monoclinic, pseudo hexagonal with the density of 2.95 gm/cc. [5]

An increase in the CA content of the cement reduces its refractoriness even when the content of aluminum oxide is high. [3] The hydration behavior of CA can be accelerated by the addition of CA_2. [14] With the increasing CA content the refractoriness of the CACs decreases even alumina content is high. [3]

B) Dodecacalcium Heptaaluminate ($C_{12}A_7$ Or $12CaO.7Al_2O_3$):-

Mayenite, $C_{12}A_7$ phase was misidentified for a long time as stable 'C_5A_3'. The structure is cubic and often shows triangular morphology in microscopic sections. [5] Under dry conditions this phase doesn't form but in presence of moisture or in ambient atmosphere it appears. [6,26] It has short initial & final setting time. Hydrates and hardens rapidly. Sometimes in small amounts it is used to control the setting rate of calcium Aluminate cements. This phase provides low strength and its melting point is given in the range of 1415 to 1490^{o}C. By controlling, lowering or raising the temperature the hydration-dehydration reaction may be reversed. [5]

C) Monocalcium Dialuminate (CA_2 Or $CaO.2Al_2O_3$):-

Calcium dialuminate (CA_2) is the secondary or auxiliary phase in CACs. It reacts slowly with water and thus setting is very slow, takes excessively long time to set. Structure of CA_2 is monoclinic based on a framework of Al_2O_4 tetrahedra in which some oxygen atoms are shared between two & others between three tetrahedra. It has been that it also occurs as natural mineral. The melting temperature of this phase is given in the range of 1700-1790^oC.

The activity of CACs with respect to hydration is known to decrease with a decrease in the ratio of C/A. [3] The hydration behavior of CA can be accelerated by the addition of CA_2, but the opposite not true, the hydration of CA_2 phase is not accelerated in the presence of CA because hydration of CA may hinder the hydration of CA_2 phase. [3,14]

D) Monocalcium Hexaluminate (CA_6 Or $CaO.6Al_2O_3$):-

It is the only non-hydrating phase in the pure calcium aluminate system and is often a reaction product in alumina castables bonded with high purity aluminate cement. It is believed that CA_6 is most readily formed in alumina castables even using CA_2 as a precursor. More recently studies on the properties and microstructure of the CA_6 phase have revealed its great potential as a strong thermal shock-resistance refractory material and its important role in the bonding of corundum and spinel aggregates. [5, 27]

2.4 Preparation of CACs by Varying Various Parameters

The formation of $CaAl_2O_4$ from $CaCO_3$-Al_2O_3 powder mixtures was studied by Iftekhar et al. [26]. They prepared $CaAl_2O_4$ phase by varying holding times between 1 & 40hr, temperature between 1300-1500^oC and in both quenched from the holding temperature. The microstructure examination showed three gray scales; darker gray corresponded to either a mixture of A & CA_2 or solely CA_2, medium gray corresponded to the main phase CA & light gray corresponded to $C_{12}A_7$. $C_{12}A_7$ was found in pockets within the main matrix of CA. mixtures of A & CA_2 was observed in porous regions of sized ranging up to ~100µm. They observed zero difference between quenched and full run samples. They found no effect on the phase fraction by the variation of holding times at lower temperatures. However for the longer holding time for higher temperatures less A & $C_{12}A_7$ & consequently more CA & constant CA_2. At higher temperatures the amount of CA phase increased as the Ca-rich phase $C_{12}A_7$ reacts with A & CA_2 to form CA.

Cristina et al [27] studied the influence of processing method on the final microstructure of reaction sintered hexa-aluminate. They have shown the following reaction sequence between $CaCO_3$ & Al_2O_3 to form CA_6:

$$CaCO_3 + Al_2O_3 \rightarrow CaO + Al_2O_3 + CO_2(g)$$

$$CaO + Al_2O_3 \rightarrow CaO.Al_2O_3$$

$$CaO.Al_2O_3 + Al_2O_3 \rightarrow CaO.2Al_2O_3$$

$$CaO.2Al_2O_3 + 4Al_2O_3 \rightarrow CaO.6Al_2O_3$$

The reaction temperatures can vary as a function of grain size, powder dispersion, forming method etc. They found that grain morphology was linked to calcium carbonate and alumina distribution in specimens. Low green densities promoted platelet CA_6 grains while high densities lead to the formation of elongated grains. Large degree of agglomeration, promoted a high porosity and low contact area, these also lead to plate formation. They found more equiaxed grains for well dispersed, low porous and high contact area. Firing temperature also affected the grain granulometry in platelet grains, with the increase in temperature they found more grown & more equiaxed grains.

A.N. Scian et al [28] studied the influence of amorphization decrease of crystallinty for the different phases present as a function milling time in the hydraulic behavior of commercial high alumina cement (CA-25). From the XRD results they found decrease in the crystallinity (peak intensity of XRD) for the different phases present as the function of milling time, taking the reference (100%) the starting material. Particle size decreases and surface increases after milling but again size increases as consequence of the agglomeration fine particles. For a water to cement ratio one (W/C=1), the ionic relation Al^{+3}/Ca^{+2} in solution is increases as function of mechanochemical treatment time. So an impact and friction milling on high alumina cement alters its crystallinity and consequently the phases richer in calcium were more affected.

In the continuation with the previous work N. Scian et al. [29] have studied the thermo mechanical properties of the mechanochemical activated high alumina cement. They found two observations from EPMA results, one is the decrease in the quantity of the quantity of Ca^{+2} and Al^{+3} ions as the milling time progresses, and the second is the increase in the ratio Al^{+3}/Ca^{+2} with the increasing milling time. But the milling time cannot be taken as an

absolute parameter because the milling also depends on different factors like kind of mill, grain size, quantity of the starting material, kind and quantity of the cement etc. that is why the crystallinity was used as the parameter for study. The early failure in mechanical behavior may be cause of that the mechanochemical activated sample showed a macropore volume much higher than the non-activated sample. The micrograph study or SEM analysis for the non-activated sample showed a crystalline needle network where in the activated sample the crystalline needle network cannot be seen, instead of that small hexagonal crystals were appeared.

V. P. Migal et al [3] studied two different set of composition of high alumina cement CA-70 & CA-73. They also described the formation of calcium aluminate in clinker takes place in accordance with the scheme-

$$C+A \longrightarrow C_3A + A \longrightarrow C_{12}A_7 + A \longrightarrow CA + A \longrightarrow CA_2 + A \longrightarrow CA_6$$

The activity of calcium aluminates with respect to hydration is known to decrease with a decrease in C/A ratio. They also described a method to regulate or control the phase composition of high alumina cement, lowering the activity of alumina by replacing part of the alumina component with the corundum makes it possible to slow the synthesis of CA_2.

They found that equilibrium mineralogical phase composition of CA-70 was 60.6% CA and 39.4% CA_2 while in case for CA73 it leads to inversion, the phase ratio decreased in the mass content of calcium monoaluminate to 39%. They also analyzed changes in ultimate compressive strength and revealed one trend as all of the concretes made with a hydraulic binder (i.e. characteristic of the specimens made with each cement): strength increased somewhat after heat treatment at 350°C, decreased after heat treatment at 800°C and firing at 1000°C, and increased at 1300°C.

2.5 Synthesis of Calcium Aluminate Phases by Different Route:-

Enrique Rocha R et al.[15] studied the reaction sintering route for synthesizing the refractory cement and also characterized the properties like density, microstructure, X-ray diffraction analysis etc. They found that refractory cement with desired properties can be obtained by using this route and at 1450^{o}C.

The synthesis reaction takes place during reaction sintering for pure Al_2O_3 & CaO was given as

$$Al_2O_3 + CaO + \Delta \rightarrow CaAl_2O_4$$

However with the increasing sintering temperature the better refractory cements can be prepared. Cement resist cooling very well below from 700^{o}C to room temperature, but from higher than 700^{o}C not resist very well and cause to damage.

J.M. Rivas Mercury et al. [16] studied the reaction sintering mechanism of $CaAl_2O_4$ phase formation by means of high energetic attrition milling of a mixtures of either α-Al_2O_3 or amorphous $Al(OH)_3$ with $CaCO_3$. They used and calculated the stoichiometry amounts from these equations.

$$CaCO_3 + Al_2O_3 \rightarrow CaAl_2O_4 + CO_2(g)$$

$$CaCO_3 + 2Al(OH)_3 \rightarrow CaAl_2O_4 + 3H_2O(g) + CO_2(g)$$

To provide maximum stability to the suspension during high energy attrition mill, they added 0.8 wt.% Dolapix-CE 64 (Carboxylic Acid, Zschimmer &Schwarz, Lanstein, Germany) and 0.1 wt.% Trimetil Hydroxyl Ammonium (HTMA).

The starting carbonate of the reactants was not eliminated by High energetic attrition milling, both batches showed a high degree of homogeneity and they behaved similarly on heating, and formed $CaAl_2O_4$ at temperature lower than 1300^{o}C. The temperatures required for the traditional solid state reaction process is usually higher than this obtained temperature.

The thermodynamic data (DSC/TG) showed the formation transitory phases. The major transitory phases were CaO, $Ca_{12}Al_{14}O_{33}$ and $CaAl_4O_7$. The nucleation and growth of $CaAl_2O_4$ took place at 1300^{o}C and showed a porous structure and small grain size (~1.5 μm).

L. A. Selyunina et al [17] studied sol gel route for the synthesis of $CaAl_2O_4$. The sol-gel method is very simple and efficient method that allows one to control the stoichiometry and phase composition of the synthesized sample and also to reduce synthesis temperature. The target product $CaAl_2O_4$ was synthesized at a 1 : 1 molar ratio between the oxide. They made an aqueous solutions of aluminum nitrate nonhydrate, calcium nitrate tetrahydrate, citric acid monohydrate and ethylene glycol. First gel was prepared and then that gel was subjected to step wise heat treatment to remove liquid phase. Finally it was Calcined in

Muffle furnace at 900-1250^{o}C. The sequence of phase formation depends on the dispersion of the initial reagents, rate of their heating in the reaction volume, their mutual diffusion and chemical interaction, nucleation and crystal growth, and crystallization conditions. DSC/TG showed few key stages in formation calcium aluminate; these stages comprised solvent removal, stepwise decomposition of the organic polymeric framework, and formation of crystalline aluminate.

XRD data showed that orthorhombic calcium aluminate accounted for 98wt% formation of the product annealed at 1000^{o}C for 1h. Minor amounts of aluminates with compositions $CaAl_4O_7$, $Ca_3Al_2O_6$, and $CaAl_{12}O_{19}$ were also identified at that temperature. 100% target phase ($CaAl_2O_4$) was obtained when the calcination temperature was increased to 1250^{o}C.

Marozova et al [18] studied a method for the preparation of calcium aluminates. They first prepared mixed Al-Ca hydroxides, and subsequently fired after pretreatment to the desired calcium aluminate. By using this method they obtained calcium aluminate phases at 300-500K lower than conventional temperatures.

They have suggested that $CaCO_3$ dissolved in the aqueous solution of aluminum chloride was a good starting material to synthesize monomineralic CA. The formation of calcium aluminate depends on C/A ration of precursor used. They adjusted the C/A ratio of the precursor by adjusting the ratio of $CaCO_3$ to $AlCl_3$. They obtained $CaAl_2O_4$ phase by using this method or from the mixed hydroxide precursors at relatively lower temperatures.

S. Yi et al. [45] studied the phase composition, Microstructure & properties of CA_6 prepared by high temperature solid state reaction at different temperatures. Lime stone and aluminum hydroxide were the starting material. Mixing, drying, die pressing and followed by high temperature sintering. With the small amounts of CA_2 and a lots of α-Al_2O_3 phases the CA_6 formed when the sintering temperature was 1400^{o}C, layered structure was also observed. The amounts of CA_6 increases while other decreases with increasing temperature. They found pure CA_6 when the sintering temperature was 1600^{o}C. The bending strength and bulk density increases and apparent porosity decreases with the increasing sintering temperature.

2.6 Additives for HAC Products

The patent no US5624489 [30] describe a method of preventing strength reduction due to phase conversion in HAC & more particularly to a method of preventing hydrogarnet (C_3AH_6) formation and promoting strattingite (C_2AH_8) formation in HAC products.

This invention described the use of siliceous pozzolanic materials, e.g. zeolite, granulated blast-furnace slag, fly ash, silica fume, rice hull ash, metakaolin, etc.; inorganic salts containing sodium or potassium cations and sulphate, carbonate, nitrate, silicate, phosphate, chloride, or bromide anion; and other chemical admixtures, in high alumina cement as additives to prevent strength reduction due to the conversion from hexagonal calcium aluminate hydrates (CAH_{10} or C_2AH_8) to cubic hydrogarnet (C_3AH_6).

The amount of these additives in the raw mixture is defined by required phase composition of the alumina cement. The addition of additives in the raw mixture makes it possible to lower the firing temperature by 300 to 350^oC depending on the quantities of these additives. The refractoriness of the high alumina cement also varies with amount and type of chloride metal used. This method succeeds to prevent formation of hydrogarnet (C_3AH_6) and promoted in formation of strattingite (C_2AH_8) HAC products and leads to no strength deterioration.

Ying Xu et al [31] in their patent no 7740066B2 studied a set of additives for the high alumina cement used in subterranean applications. When high alumina cement alone is used for subterranean applications it shrinks in volume. To overcome this problem or drawback a set of composition for this application is studied and results of this invention shows the favorable shrinkage profile or it may expand during setting. The invention concluded successfully by using the additive (comprise 80-99wt% of siliceous pozzolan & 1-20wt% of an inorganic Na or K salt) and also simultaneously the formation of hydrogarnet was significantly reduced.

W. C. Oliver et al. [32] studied a composition of HACs which has thermal stability over a wide temperature range and which develops strength at early age. The principal characteristics of high alumina cement are development of very high or maximum strengths at early ages. The resistance to corrosion in sea or sulfate water and resistance to weak solutions of mineral acids are outstanding. However at higher temperatures the strengths drops off rapidly. This can be prevented by using calcium sulfate into the cement; however it

lowers the heat of hydration of the system thus limiting the application of cement to lower temperatures.

The present invention disclosed the composition which has thermal stability over a wide temperature range and which develops strength at early age. This composition comprises high alumina cement a halide salt & calcium sulfate sodium chloride, potassium chloride and lithium chloride are preferred salts. The resultant composition of this invention can be used or employed in environments subject to wide temperature range without strength variation or drop with thermal variation.

C. parr et al. [33] studied a reaction controlled calcium aluminate technologies for deflocculated castables. The need of greater robustness to placing variables like ambient temperature and more predictable behavior in terms of the workability and hardening relationship. In this work they developed a new process which aims to modify the reactivity of this phase and its interaction with the other calcium aluminate phases. The ultrasonic, exothermic and vibration profile suggests that Reaction controlled CAC follows a different hydration kinetic/mechanism.
Vibration flow and early strength examination also showed that RC CAC suggests a real demoulding time of only a few hours after casting. This development allows an intrinsic control for the development of new calcium aluminate binders offering a modified tradeoff between extended working times but without delaying the acquisition of sufficient mechanical strength for demoulding.

2.7 Hydration of HAC's:-

Claudia M. M. Freitas et al [11] studied formation of different hydrated phases and their microstructure, formed at different temperatures. Previous works reported the following calcium aluminates hydration products of CA or CA_2: CAH_{10}, α-C_2AH_8, β-C_2AH_8, C_4AH_{13}, $C_4A_3H_3$, C_4AH_{11}, C_5AH_{34}, $C_4AH_{12\text{-}14}$, CAH_7, $CAH_{10\text{-}12}$, C_3AH_6, etc. Out of these, only CAH_{10}, C_2AH_8, and C_3AH_6 are stable at room temperature. Hydration of $C_{12}A_7$ leads to C_2AH_8, which then slowly changes into C_3AH_6. They showed that for 70%wt cement hydration at 6^oC, CAH_{10} in euhedral hexagonal plates and small amounts of crystalline AH_3 were identified whereas for 80%wt cement more crystalline phases were identified. Like CAH_{10}, AH_3, C_3AH_6 and traces of C_2AH_8. For 70%wt cement hydration at 20^oC, reacted more quickly with water, less CA & CA_2 present than at 6^oC; and more crystalline phases

produced CAH_{10}, $C3AH_{8-12}$, C_3AH_6 and AH_3 were identified whereas for 80%wt cement more crystalline phases were identified. Like CAH_{10}, AH_3, C_3AH_6, C_3AH_{8-12} and C_2AH_8. The hydration was incomplete, more anhydrous Calcium Aluminates were present and α-Al_2O_3 not reacted or hydrated at this temperature. At 60^oC, Crystalline AH_3 was observed as the main hydration product along with C_3AH_6 and C_3AH_{8-12} also occurred for both cements.

M. R. Nilforoushan et al. [34] described the role of different phases present in the calcium aluminates cement on their hydration reactions and application properties in castables. They showed that a large amount of $C_{12}A_7$ in the cement shows flash setting behaviors in slurry. The calcium aluminates cement with lower Blaine value affects the setting time of cement due to longer intrusion time required for penetration of water into the grains of cement. With the decreasing C/A ratios or large content of higher alumina containing phases the flash setting disappears.

C. Alt et al. [35] have showed the hydration behavior of the calcium aluminate cement. They managed to describe that during the hydration of the most reactive phases of calcium aluminate cement, heat is generated increasing the cement paste temperature and promoting the reaction even of the most inert phases. As shown in the figure, the hydration process of calcium aluminate cement occurs in three steps. When the hydration of calcium aluminate begins, a small temperature increase was observed (region I, Figure 2.1), this is followed by a dormant period (region II). The third region of the hydration profile shows that hydrate precipitation is followed by an increase in the heat released (region III).

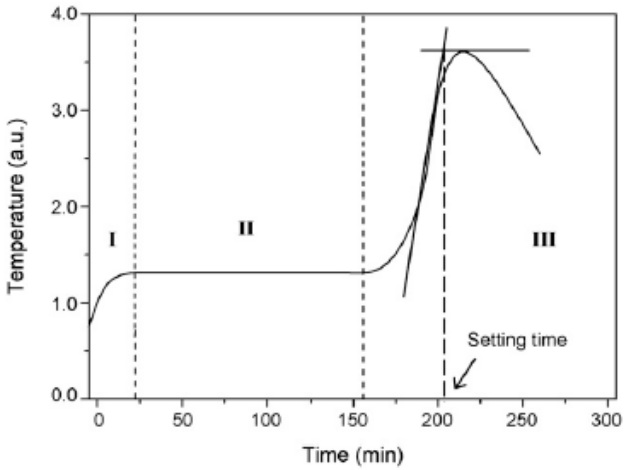


Fig. 2.1. Schematic representation of temperature profile in arbitrary units (a.u.) as a function of time for a CAC suspension.

Alain Campas et al [36] studied about the hydration behavior of the high alumina cement with varying the temperature. They found that hydrates formed at a very low temperatures are CAH_{10} with very little AH_3. When temperature was increased progressively, C_2AH_8 & AH_3 gel were formed and the amount of CAH_{10} present was decreased. At about 30^oC that crystallized CAH_{10} completely disappeared and that only C_2AH8 & AH_3 precipitated. At further higher temperatures, at 50^oC, C_3AH_6 and AH_3 were formed directly without formation of other phases.

Steffen Mijhmel et al [37] studied the influence of alumina reactivity on the hydration behavior of mono calcium aluminate, and concluded that the addition of alumina to mono calcium aluminate influence its hydration behavior and with high surface areas of alumina leads to shorter induction period on the hydration. Additionally higher Na_2O content also leads to shorter the induction period during hydration.

2.8 Dehydration of HAC's:-

During the heating, the bond phase undergoes various transformations. After casting & during drying or heating at 110^oC, the incomplete hydration continues to completion; crystallized gibbsite phase appears.

AH_3 & C_3AH_6 gradually decomposes to amorphous anhydrous and water vapor at or in between 100-400^oC. Porosity increases and strength decreases. In temperature range between 400-900^oC, subsequent dehydration of stable hydrates C_3AH_6 dehydrates to $C_{12}A_7$ & gibbsite transforms to alumina hydrate. Porosity continues to increase and strength also to decrease. In region between 800-1100^oC, porosity max & strength tends to minima, bonding phase first re-crystallize to $C_{12}A_7$ then CA from 950^oC onwards CA_2 formation begins. At about 1100^oC CA_2 reaches maximum.

In case of 80% Al_2O_3 HAC's above 1300^oC CA_6 form from CA_2 and Al_2O_3. Above 900^oC, CA crystallized and sintering began to occur and this led to ceramic bonding and improves strengths. [14]

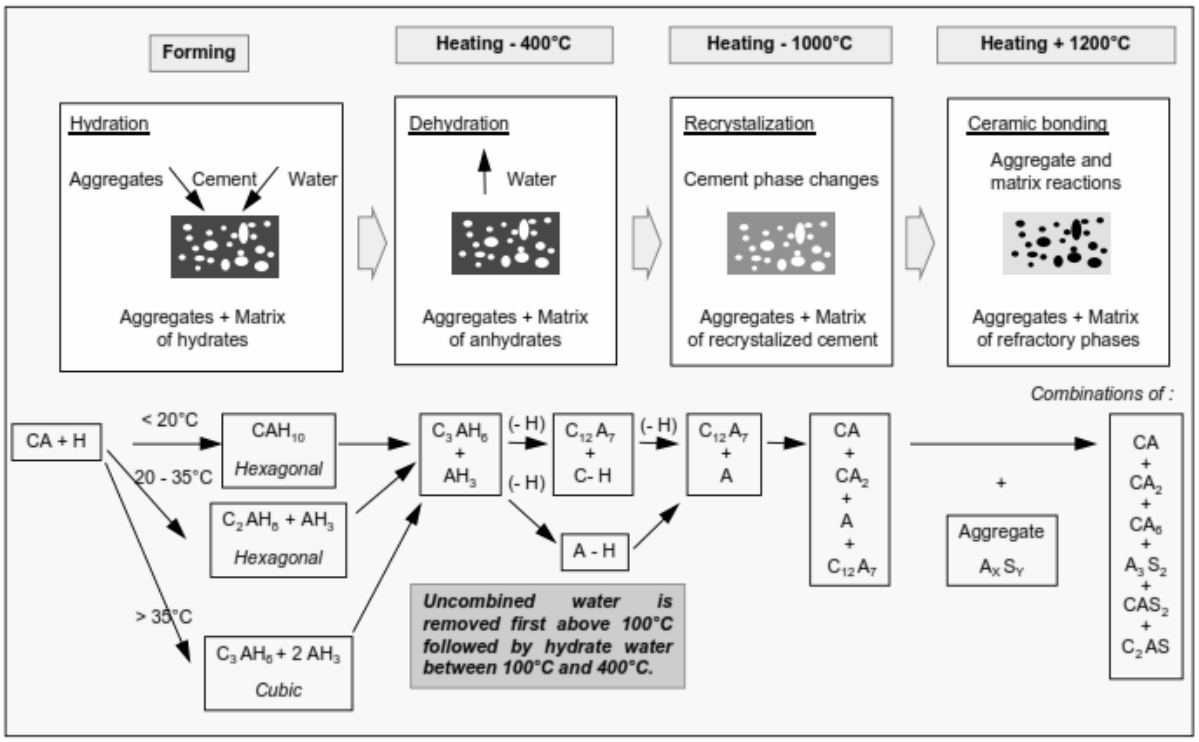
C. Parr et al. [40] described the hydration/dehydration process of calcium aluminate cement in castables, shown in fig. .The amount of $C_{12}A_7$ increases dramatically up to 800°C, after which it is slowly consumed as CA and CA_2 become more prevalent with higher temperature. Thus as the CA hydrates dehydrate, a recrystallization takes place which first forms $C_{12}A_7$

followed by stable anhydrous phases. This is typical of the mechanisms that take place in conventional castables and explains why there is a loss of strength at intermediate temperatures before ceramic reactions start to occur at high temperature.

S. Maitra et al. [38] studied the dehydration kinetics of calcium aluminate cement. The hydration of calcium aluminate cement follows multistage dehydration with different reaction orders at different stages at different different temperatures. Author described different dehydration stages in CAC during heating. The stages were described as: (i) Removal of surface bonded water, (ii) Dehydration of aluminum hydroxide gel, (iii) Dehydration of CAH_{10} to $C_2AH_{8,}$ (iv) Dehydration of C_2AH_8 to C_3AH_6 & (v) Dehydration of C_3AH_6 to anhydrous CA. The progressive collapsing of layers as a result of dehydration probably increased the activation energy for dehydration at the initial stage, but afterwards the disintegration of the lattice at elevated temperatures caused a reduction in activation energy.

During heating of refractory castable, hydration product undergo conversion& dehydration. At temperature between 900^{o}C & 1100^{o}C the strength decreases and reaches to a minimum value. At higher temperatures, strength & resistance to abrasion increases. Sintering reactions between the cement & aggregate and ceramic bonding are the reason behind this strength development in castable. On the basis of compositions of the cement & aggregate, the compounds formed include high melting phases as CA_2, CA_6 spinel. [19]

Fig. 2.2 The hydration/dehydration process



H G Midgley et al [9] studied the relation between mineralogical phase composition and strength development in high alumina cement. Pleochroite phase gives a high strength, but not as high as is obtained from CA, but the strength development is much slower. The mineralogical composition of high alumina cements (HAC) will considerably affect the strengths of concretes made from them. HAC's are likely to contain CA, $C_{12}A_7$, C_2AS, CT, ferrite solid solution (C_2F-C_2A), FeO, C_2S and the calcium iron aluminate silicate, pleochroite. CA and pleochroite are the major hydratable constituents, though $C_{12}A_7$ and C_2S may also contribute to the strength. They obtained that 1 day strengths of cements cured at 18°C tend strongly to increase with CA content, though the cement with 43.2% of CA gave a stronger product than that with 60.3%. This may be of cause that CA is primarily but not exclusively responsible for the early strength. At later ages, the strengths obtained with cements cured at 18°C also tend to increase with CA content, but the differences become less marked with increasing time, and at 28 days the cements high in pleochroite gave strengths nearly as high as those high in CA. The cements high in CA showed the expected progressive strength loss with time on curing at 50°C, attributable to conversion. Those high in pleochroite behaved similarly, but the effect was relatively less and the 3-day converted strengths were higher than the strengths obtained on curing for 1 day at 18°C. Pleochroite gives ultimate strengths only slightly lower than those obtained with CA, but that the rate of strength development is lower.

Karen L. Scrivener et al. [39] studied corrosion and abrasion resistance of calcium aluminate cements based refractory castables. They showed that on reaction with water, any calcium aluminate phase form hydrates and it is an exothermic process. They observed that calcium aluminate cement hydrates shows better resistance to acid attack and possess good abrasion resistance. Control of the initial water-to-cement (w/c) ratio is very important to ensure that the minimum strength is sufficient for the application. Strength increases continuously as the conversion reaction in the hydrated phases proceeds.

Chapter-3

Experimental Procedure

3.1 Materials & Compositions

The research work was carried out in two stages. In the first stage high alumina cements were prepared in lab scale & they were studied chemically & mineralogicaly and then in the next stage those cements were utilized in making castables and characterization of those castables were done. Calcareous & aluminous sources used for the preparation of different types of HAC's are hydrated lime, calcined alumina, white fused alumina and reactive alumina. The raw materials used for the preparation the castables are white fused alumina (WFA), andalusite, calcined clay, reactive alumina, microsilica, sodium hexa-metaphosphate (SHMP), and aluminum powder. Self-prepared HAC's were used to make these castables. The details chemical analysis of the raw materials was done at OCL INDIA Ltd, Rajgangpur and the results were given in table-4.

Table 3.1. Chemical Analysis of Raw Materials used

Raw materials	Al_2O_3	SiO_2	CaO	Fe_2O_3	TiO_2	K_2O	Na_2O	MgO	LOI
Hydrated lime	-	Trace	72.55	-	-	-	-	-	25.72
Calcined alumina	97.01	Trace	-	0.05	Trace	-	0.18	-	0.72
WFA	98.33	Trace	-	0.04	Trace	-	0.52	-	0.46
Reactive alumina	98.89	Trace	-	-	-	-	0.07	-	0.40
Calcined clay	38	53	0.62	1.08	1.84	0.03	0.03	-	-
Micro silica	0.4	97.89	0.15	0.10	Trace	0.20	0.10	0.30	1.01
SHMP	-	-	-	-	-	-	34.8	P_2O_5= 65.2	
Al powder	Al metal= 99.48								

Six different types of compositions were selected for the preparation of HAC's, but out of these only six compositions were chosen for further investigation. So here in the table 3.2 detailed compositions of only those six HAC's are given. All the prepared HAC's were sintered at two different temperatures (1430^{o}C & 1470^{o}C). So now we have two different classes of HAC's of the same composition.

Table 3.2. Composition of Different High Alumina Cements (HAC's) prepared

Composition	Source used	A	B	C	D	E	F
CaO	Hydrated Lime	30	25	20	28	28	28
Al_2O_3	Calcined Alumina	70	75	80	72	67	67
	WFA	-	-	-	-	5	-
	Reactive Alumina	-	-	-	-	-	5

The prepared HAC's was then used to make castables. Out of these six only last three HAC's were used to make castables and each HAC's composition has two classes. So the number of prepared total castables was eight. The weight percent of cement used was made invariant. Table 3.3 shows the weight proportion of different raw materials used for making castables.

Table 3.3. Composition of Castable

Raw Material	wt%
WFA (-200)	05
Reactive alumina	7.5
Mulcoa (0-1)	21
Andalusite (-200)	10
Andalusite (3-8)	10
Andalusite (1-4)	30
Calcined clay (3-6)	10
Micro silica	04
SHMP	0.05
Al Powder	0.50
HAC's (self-prepared & imported)	02

3.2 Stage-1 Preparation of HAC's

3.2.1 Batch Preparation:-

Calcined alumina, white fused alumina, reactive alumina and hydrated alumina were used for the preparation of different HAC's. As composition given in table… the required raw materials were weighted and mixed homogeneously for the uniform distribution of materials. Each batch was prepared of 2kg.

3.2.2 Nodules Formation:-

The mixed batches were then moistened by adding water and then again mixed uniformly. Better to say the mixed batch was kneaded very well. After that the nodules of diameter 10-15mm were made by hand rolling method.

3.2.3 Drying:-

Prepared wet nodules were then kept for drying. Usually sun-drying is used for the drying of HAC nodules, so herein also natural drying was done for at least 72hr for each batch.

3.2.4 Sintering:-

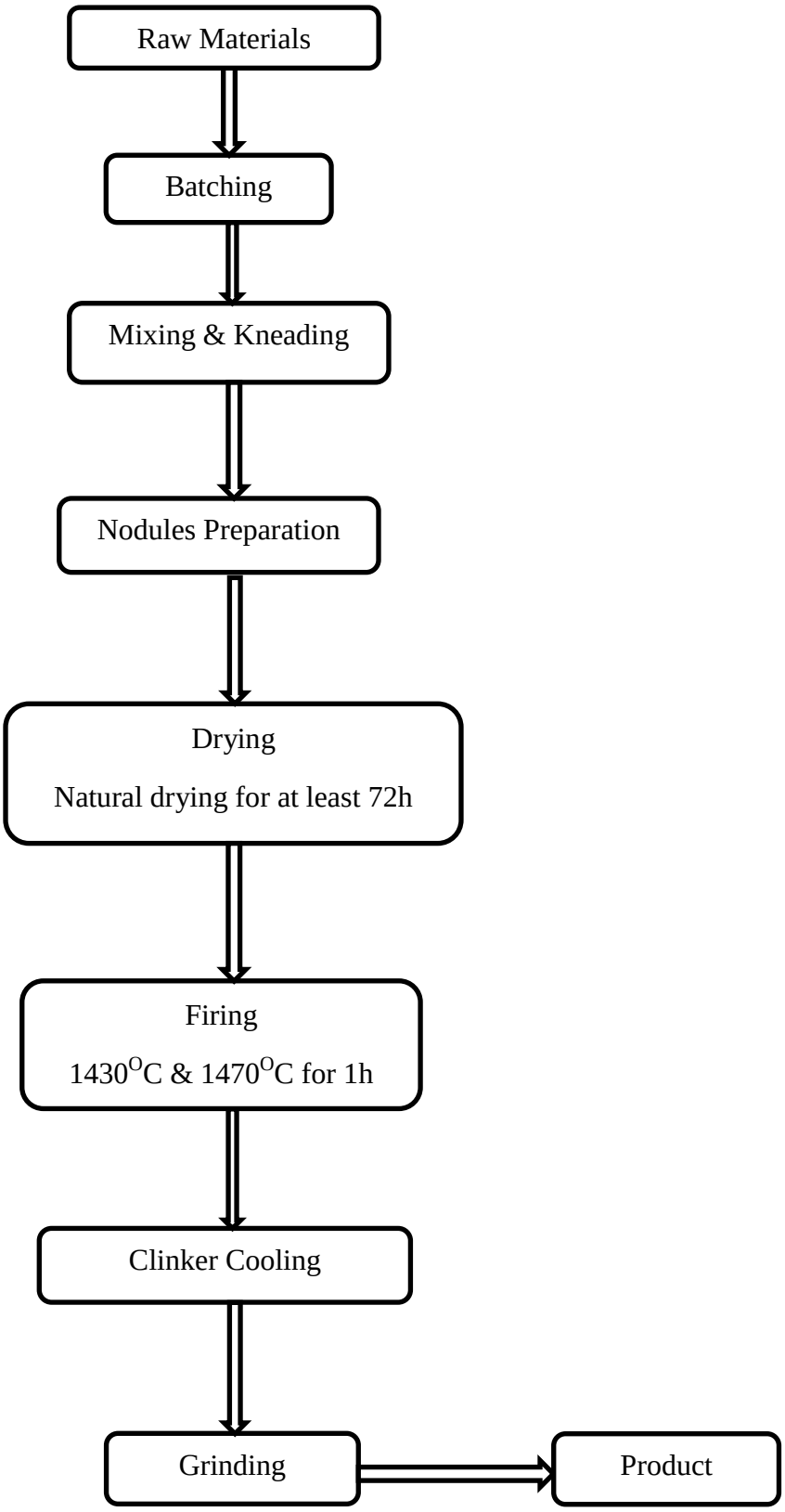
The prepared dried nodules were then sintered in electrically operated laboratory furnace. Mullite & High-alumina trays were used to place the nodules inside the furnace. Tray was selected over cup type crucibles to maintain uniform temperature distribution along length as well along height. Sintering was done at two temperatures 1430^{o}C & 1470^{o}C for soaking period of 1hr at the rate of 5^{o}C/min.

3.2.5 Clinker Cooling & Grinding:-

Sintered nodules or say clinkers were then cooled to room temperature and then ground to cement fineness. First mortar pestle was used to reduce the size of clinker and then ground finely by milling in lab scale vibro grinding mill (Herzog HSM100H).

After grinding characterization part of prepared cement was carried out.

Fig. 3.1. Flow Chart for preparation of HAC (Lab Scale)



3.3 Stage-2 Castable formation using self-prepared cements

3.3.1 Batching

In the following work next to preparation of HAC & their study, castable of those HAC's were prepared and investigated. 10kg of each castable was made of composition as given in Table . The batches were prepared by taking different grade of materials in proper proportion. Each batch contains 10kg of materials. The materials were dry mixed in a pan mixer of 30kg capacity (rpm-32) for 25 minutes.

3.3.2 Mixing

Wet mixing of castable mix was performed after the dry mixing. To achieve the desired rheology in ULCC generally 5wt% water is required. Practically a two-step water addition method was followed to achieve the desired rheology and flowability & was as follows:

First two third proportion of water was added at a time. The other one third of water was then added slowly to get homogenous or uniform mixing. Up to 5-6 minutes the wet mixing was performed to achieve proper flow. Vibration flow value is represented by flowability & is measured using the flow cone with 50mm high, 100mm base diameter, and 70mm top diameter.

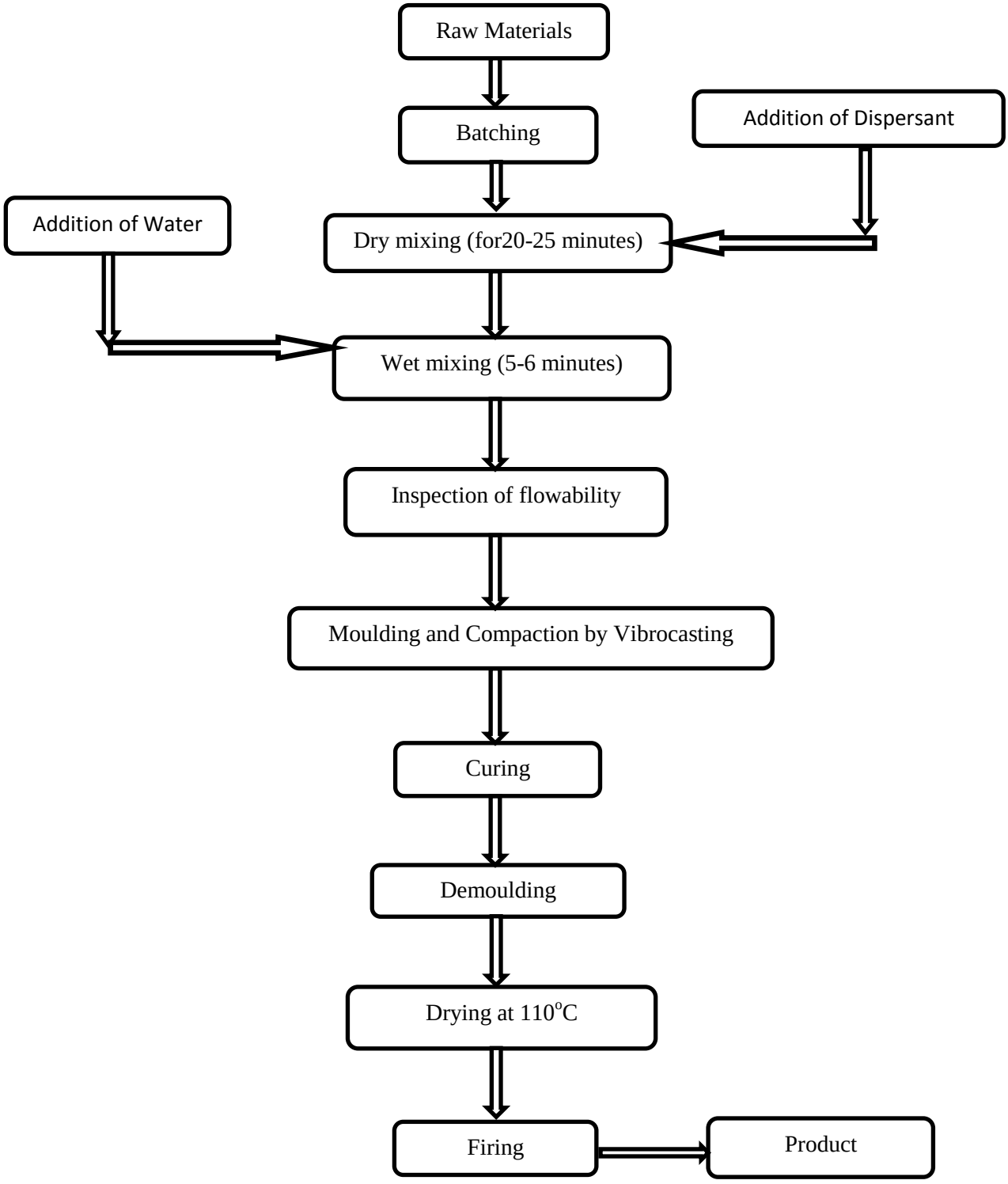
On a vibration table working at 50 Hz of frequency and amplitude of 0.5mm the flowability testing was performed. The castable mix was filled into the cone, just after wet mixing. The cone was placed in the vibrating table (according to ASTM norm Cone 240 C) filled with the castable.

After that cone was removed and castable was subjected for vibration for 20 seconds and allowed to spread. The ultimate diameter of the "spread cone" or "cake" was measured in millimeters & was taken as the vibration flow value.

3.3.3 Casting

The mixed castable was then poured into the lubricated molds of 160x40x40mm onto a vibrating table with 50Hz vibrating rate. By a trowel the excess mix was scrapped off and smoothened the outer surface. The molds were kept for 24 hours in humid condition to avoid the immediate drying of the surface or say cured in a moisture saturated environment. For each composition eight bar samples were prepared for laboratory testing. The detail of the sample preparation procedure is given the Fig. 3.2. After that the samples were demoulded and dried in oven at 110^{o}C for 24 hours.

Fig. 3.2. Flow chart for preparation procedure of castable



3.3.4 Drying

After curing process completed, the prepared bars were de-molded and placed in an oven at 110^{o}C for 24h for drying.

3.3.5 Firing

Dried samples were then fired in electrically operated laboratory furnace at three different temperatures. Samples were fired at 800 ^{o}C, 1400 ^{o}C and 1600 ^{o}C with soaking time 2hours. After completion of firing of samples, characterizations of samples were done.

3.4 Evaluation of properties

The chemical and mineralogical properties of self-prepared cements have been evaluated. The chemical analysis was done in the usual test procedure. For the mineralogical or phase identification, X-Ray Diffractometer (PW-1830, Philips, Netherlands made) using Cu K-α radiation was used. The physical and mechanical properties namely bulk density (BD), cold crushing strength (CCS) and cold modulus of rupture (CMOR) of dried casted samples as well as samples fired at 800^{o}C, 1400^{o}C and 1600^{o}C have also been evaluated. The chemical analysis of the castable was supplied by the industry.
For the testing of above mentioned parameters the procedure adopted are as follows:

3.4.1 Determination of Bulk Density of the Castable

Bulk Density (B.D) is the ratio of the mass of the dry material of a porous body to its bulk volume. The bulk density is a measure of weight per unit volume and depends upon true specific gravity and the porosity. It is expressed in g/cm3 or in kg/m3
The Archimedean method is used to find Bulk Density. For the measurement of Bulk Density, the test piece (65 × 65 × 40 mm) is dried at 110ºC to constant mass, weighed in air, and then transferred to airtight vacuum chamber, which is then evacuated until a minimum pressure is reached. After the vacuum is maintained for a set time period, water is poured until the specimens are completely covered and to ensure open pores are filled. At

atmospheric pressure, the specimens are reweighed while suspended in the liquid to determine the apparent mass, and then finally the soaked test piece is reweighed in air.

$$\text{Bulk Density} = \frac{\text{Mass in air}}{\text{Soaked Mass - Suspended Mass}} \times \text{Density of liquid (water)}$$

Unit of Bulk Density- gm/cc

3.4.2 Cold Crushing Strength (CCS)

A mechanical compression testing machine (UTM) was used to determine the cold crushing strength of the test specimen. 75mm cube test specimen was dried at 110ºC and then cooled to room temperature. The load was applied on the sample in the flat position. The load was applied uniformly until the specimen failure.

Cold Crushing Strength = (Load / Area)

Load in Kg and Area in cm^2

Cold Crushing Strength, in Kg/cm^2

3.4.3 Cold Modulus of Rupture (CMOR)

CMOR is measured as the maximum stress that a rectangular test piece can withstand when it is bent in a three-point bending device. The test specimen was kept horizontally in a support having two edges and then load was applied on the sample uniformly during the test at a rate of 1.25 Kg per minute. The load (W) at the specimen failure was noted and modulus of rupture of the specimen was calculated from the formula:

$$CMOR = \frac{3WL}{2bd^2}$$

Where L is the distance between bearing edges (cm); b is the width of specimen (cm); d is the thickness of the specimen (cm).

3.4.4 Phase Identification (X-RD)

For X-ray diffraction (XRD), the samples were crushed and ground. Then it was packed in a sample holder specially designed for x-ray diffractometer. The sample was inserted in to the XRD machine. The XRD patterns were recorded on a unit (Philips PAN Analytical, The Netherland Electronic Instruments) using Ni-filtered Cu-Ka (λ = 1.54056Å) radiation working at 25 mA and 35 kV.

Measurements were done on sample rotating at 4degree per minute in the interval 20-70 degree (2θ). After that phase analysis and quantification of different phases present in the self-prepared HACs were examined. The obtained diffraction patterns were smoothened, fitted and analyzed using Philips X-pert high score software. The semi quantitative phase analysis was done by Phillips JCPDS software of all self-prepared cements.

Chapter-4

Results & Discussion

4.1 Results & Discussion

As described earlier that work was done in two stages, first preparation of HACs by varying composition & firing temperature and second those cements were used in making refractory castables. Characterization of both cements and castables were done separately. The chemical analysis of all the raw materials used in the preparation of HACs & castable was done in lab at OCL, Rajgangpur. After the preparation of HACs they were examined chemically & mineralogically. For the mineralogical study, cement powders were characterized by XRD for phase analysis & quantification of different phases present. Properties like Apparent porosity, bulk density, cold compressive strength, and cold modulus of rupture were investigated or measured of prepared castables.

4.2 Characterization Self-prepared HACs

4.1.1 Chemical Analysis of Cement

Calcareous & aluminous materials are the main raw material group for the preparation of HACs. So the major constituents of any HACs must be CaO & Al_2O_3. As shown earlier (Table), the Al_2O_3 content in CACs varies from about 35 to 80%and the lime content varies ~16 to 40%. Table 4.1 summarizes the chemical analysis result of all the self-prepared cements. Chemical analysis of all cements was performed in usual & standard method of testing. It has been found that the only C-group of cements contains ~80% Al_2O_3, as their starting composition was 80:20: Al_2O_3: CaO. It was found that all types of cement contain a very trace amount of Fe_2O_3.

Table 4.1 The Chemical Analysis Result of All The Self-Prepared Cements.

Type of Cement	Al_2O_3	CaO	Fe_2O_3
A/1430	70.25	28.59	0.16
A/1470	70.97	26.20	0.16
B/1430	69.06	28.11	0.26
B/1470	72.01	26.06	0.24
C/1430	80.79	18.69	0.18
C/1470	78.92	18.51	0.12
D/1430	71.34	27.18	0.44
D/1470	70.55	27.55	0.30
E/1430	70.18	27.92	0.56
E/1470	69.9	28.29	0.34
F/1430	71.56	27.18	0.35
F/1470	71.15	27.18	0.37

4.1.2 Mineralogical Analysis

The XRD analysis of cements was done on a unit (Philips PAN Analytical, The Netherland Electronic Instruments) using Ni-filtered Cu-Kα (λ = 1.54056Å) radiation working at 25 mA and 35 kV. The obtained diffraction patterns were smoothened, fitted and semi quantitatively analyzed using Philips X-pert high score software. The phase identification was done by Phillips JCPDS software. Table shows the percent of different phases present in all types of cements.

The XRD pattern of Group-A cements are shown in the Figure- 4.1 & 4.2. It is observed that Group-A cements contain CA & CA_2 phases only. The major phase present in A-Type cement fired at 1430^{o}C is CA which accounts ~72% (according to semi-quantitative analysis) and CA_2 content is ~28%. CA phase content decreases to ~59% when the cement was fired at 1470^{o}C and content of CA_2 phase increased to ~41%. The decrease in CA & increase in CA_2 phase shows the reaction proceeds to completion is more for higher temperature fired cement. As the firing temperature was increased more Al_2O_3 reacts with CA phase and forms more CA_2 phase instead of only forming CA. CA is the most important phase and principal hydraulic compound presence in the calcium aluminate cements. CA phase generally occurs in 40-70% and this phase has high melting point and it melts congruently at 1600^{o}C. It is estimated that higher percentage of CA phase may be responsible for high strength, low refractoriness & earlier hydration in Group-A cement fired at 1430^{o}C whereas 1470^{o}C fired cement may show low strength, better refractoriness & later hydration due to higher percent of CA_2 present. [3,13]

Fig.4.1 XRD analysis of Cement A fired at 1430^{o}C

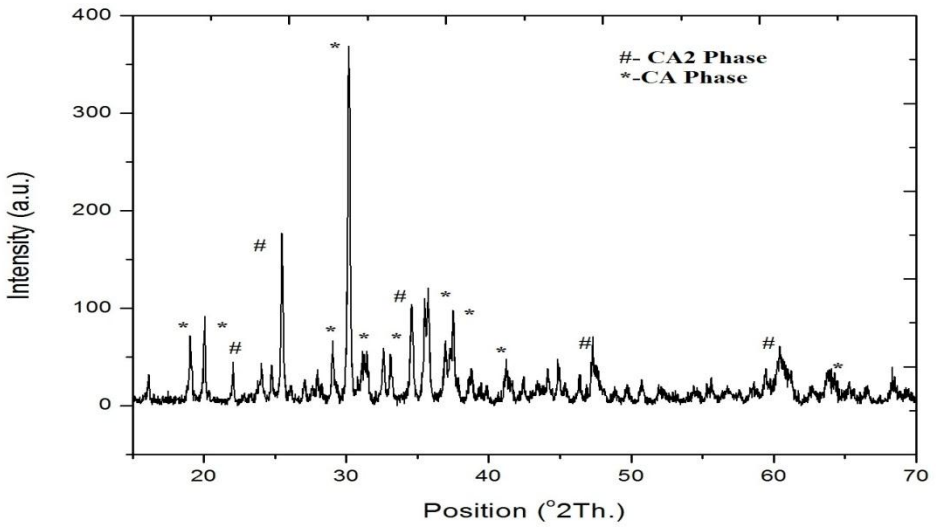
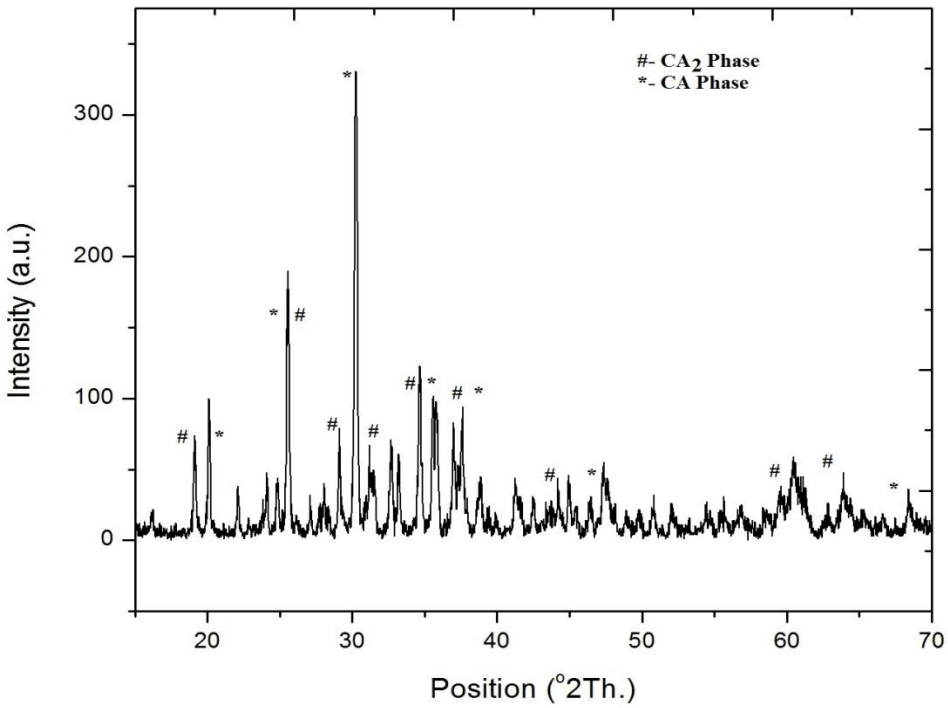


Fig.4.2 XRD analysis of Cement A fired at 1470^{o}C



The XRD patterns of Group-B cements are shown in the Figure- 4.3 & 4.4. Here as the alumina content is higher 75% comparing to previous group cement where alumina content is 70% so correspondingly CA phase quantity decreases and CA_2 phase content increases. It is observed that the major phase present in this cement fired at 1430^{o}C is CA which accounts ~55% (according to semi-quantitative analysis) and CA_2 content is ~45%. CA phase content decreases to ~41% and content of CA_2 phase increased to ~59% when the cement was fired at 1470^{o}C. The decrease in CA & increase in CA_2 phase shows the reaction proceeds to completion is more for higher temperature fired cement. As the firing temperature was increased more Al_2O_3 reacts with CA phase and forms more CA_2 phase instead of only forming CA. CA_2 reacts slowly with water and thus setting is very slow, takes excessively long time to set. So it may be predicted that this group of cement may show poor hydration behavior. [3]

Fig.4.3 XRD analysis of Cement B fired at 1430^{o}C

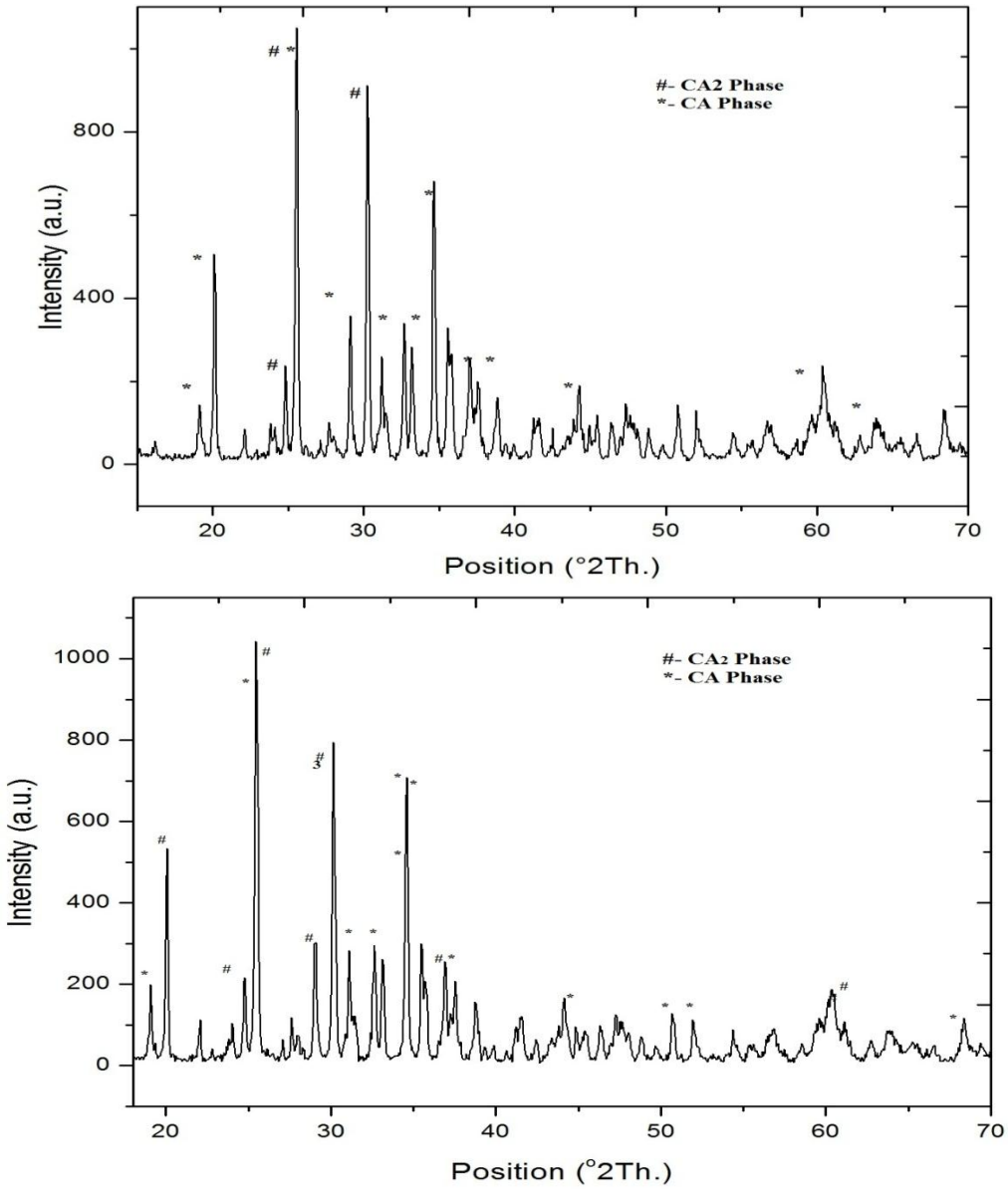
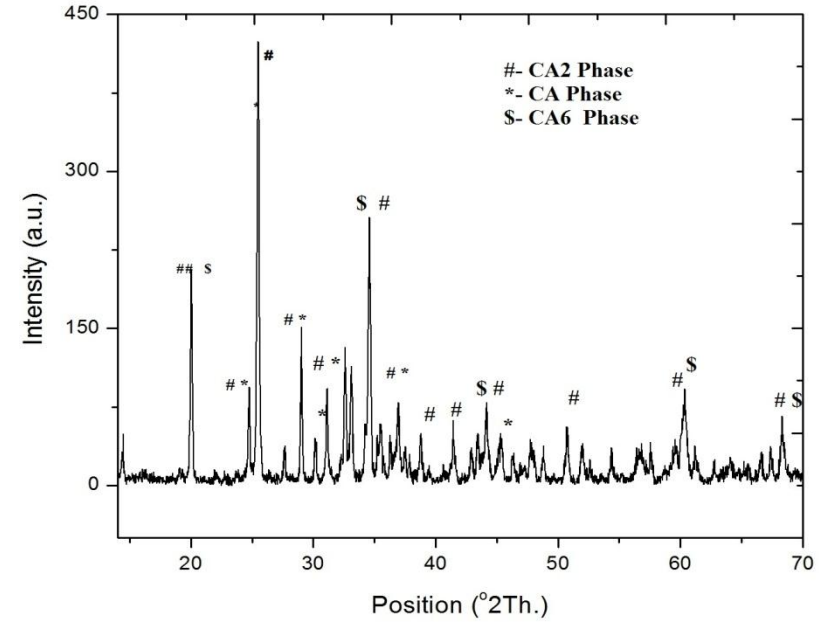


Fig.4.4 XRD analysis of Cement B fired at 1470^{o}C

The XRD patterns of Group-C cements are shown in the Figure- 4.5 & 4.6. This is 80% alumina containing cement so the trend of increasing CA_2 phase and decreasing CA phase is more prominent here. It is observed that this cement contain CA_6 phase along with CA & CA_2 phases. The presence of CA_6 phase may be due to the higher alumina content around 80% in this group of cement. The major phase present in this cement fired at both temperatures (1430^{o}C & 1470^{o}C) is CA_2. This accounts ~70% (according to semi-quantitative analysis. CA & CA_6 phase content is ~12-16%.

Fig.4.5 XRD analysis of Cement C fired at 1430^{o}C



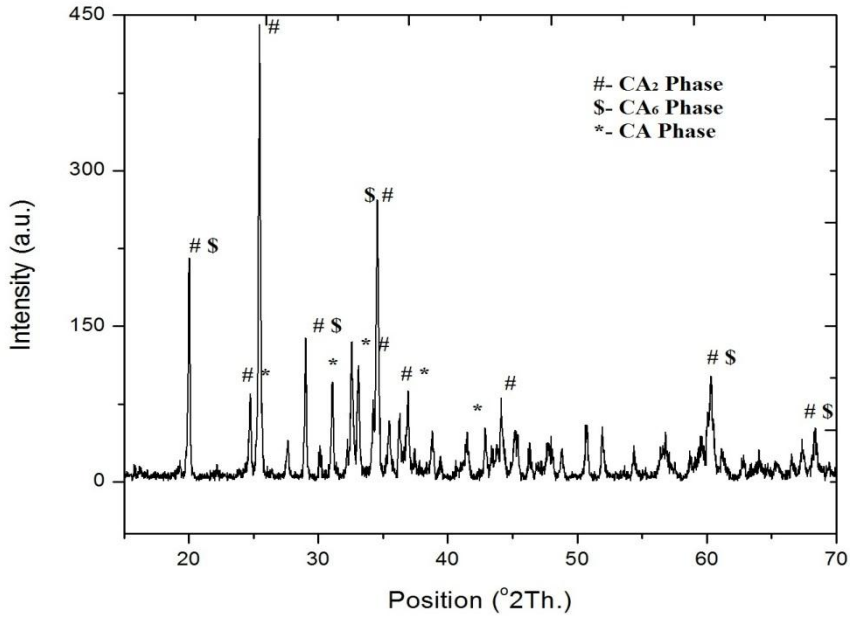
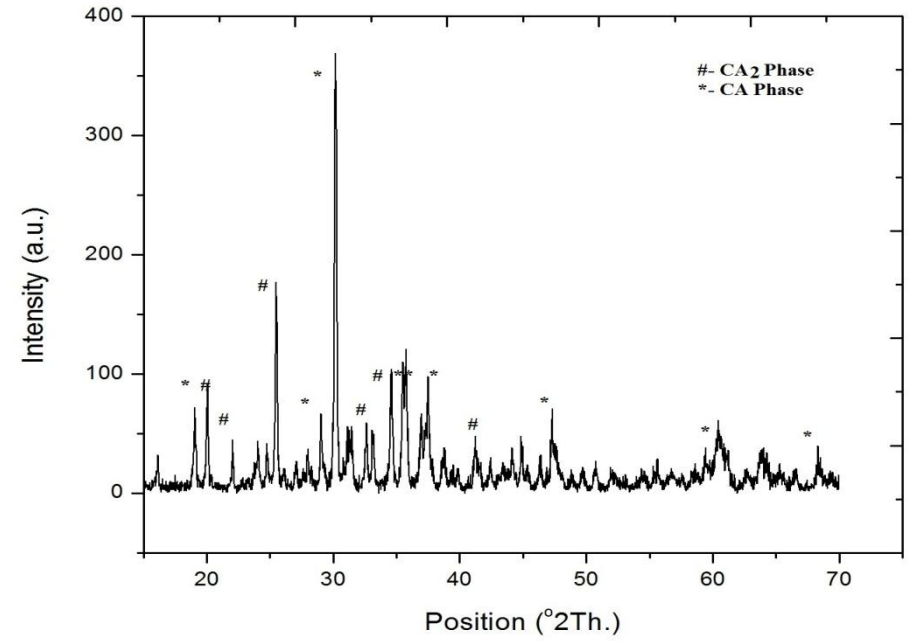


Fig.4.6 XRD analysis of Cement C fired at 1470^{o}C

The XRD patterns of Group-D cements are shown in the Figure- 4.7 & 4.8. It is observed that Group-D cements contain CA & CA_2 phases only. The major phase present in D-Type cement fired at 1430oC is CA which accounts ~74% (according to semi-quantitative analysis) and CA_2 content is ~26%. CA phase content decreases to ~66% when the cement was fired at 1470^{o}C and content of CA_2 phase increased to ~34%. The reason behind this decrease in CA & increase in CA_2 phase with temperature is same as in earlier case. CA is the most important phase and principal hydraulic compound presence in the calcium aluminate cements. CA

phase generally occurs in 40-70% and this phase has high melting point and it melts congruently at 1600^{o}C. It is estimated that higher percentage of CA phase may be responsible for high strength, low refractoriness & earlier hydration in cement fired at 1430^{o}C whereas 1470^{o}C fired cement may show low strength, better refractoriness & later hydration due to higher percent of CA_2 present in it. [3]

Fig.4.7 XRD analysis of Cement D fired at 1430^{o}C



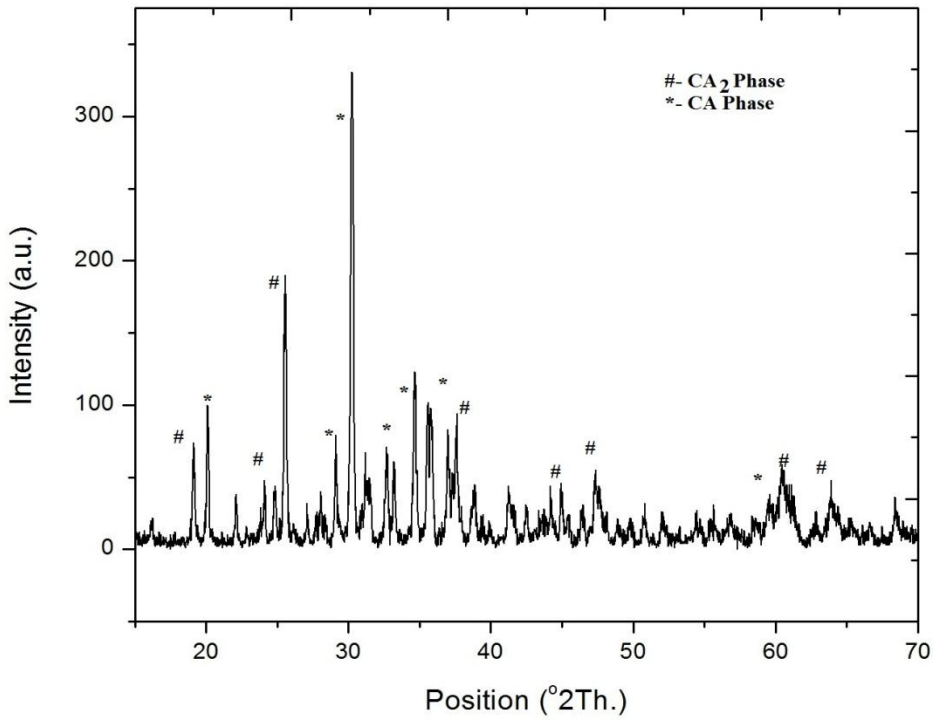
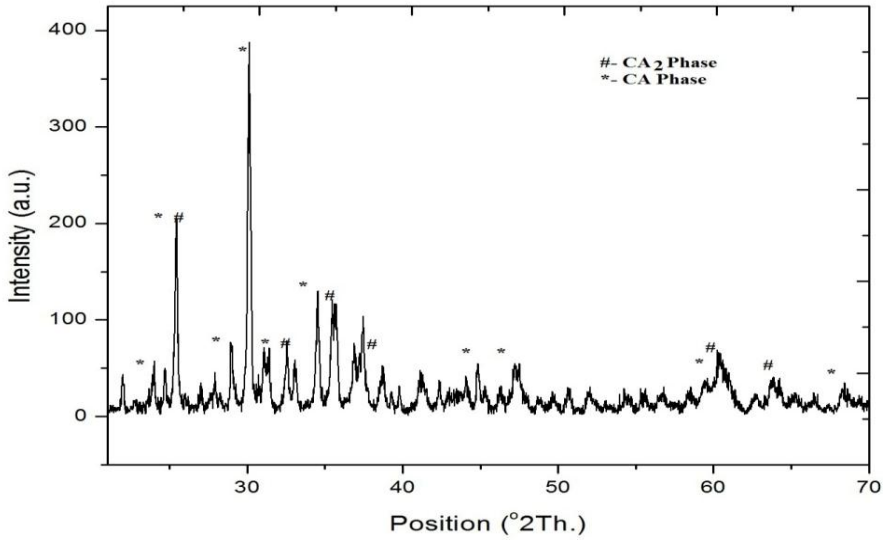


Fig.4.8 XRD analysis of Cement D fired at 1470^{o}C

The XRD pattern of Group-E cements are shown in the Figure- 4.9 & 4.10. It is observed that Group-E cements contain CA & CA_2 phases only. The major phase present in E-Type cement fired at 1430^oC is CA which accounts ~71% (according to semi-quantitative analysis) and CA_2 content is ~29%. CA phase content decreases to ~65% when the cement was fired at 1470^oC and content of CA_2 phase increased to ~35%. It is very similar to the Group-D cement because both in group-D and group-E cement batch the alumina content is same that is 72% the only difference is that in group E cement 5% of alumina was replaced by WFA. Since WFA is a purer variety of material compared to calcined alumina so in this batch CA_2 phase content is slightly higher.

Fig.4.9 XRD analysis of Cement E fired at 1430^oC



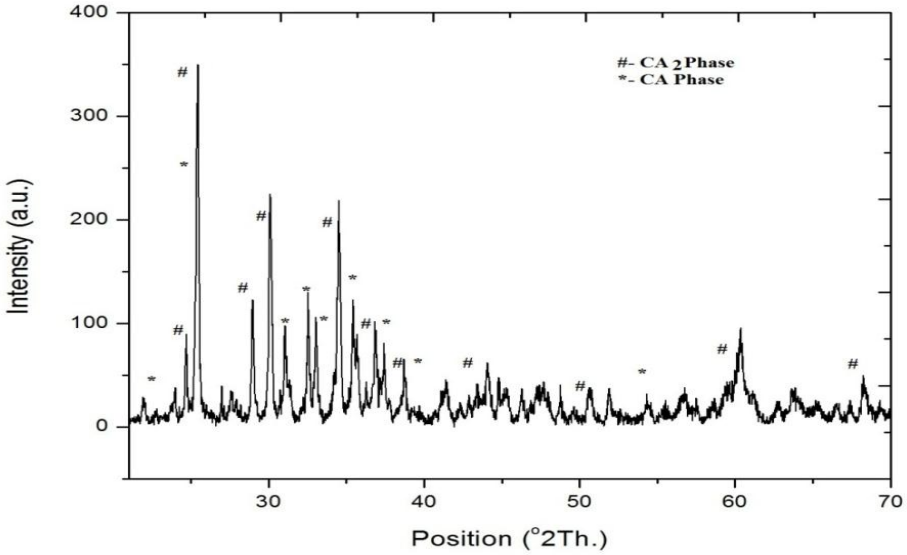
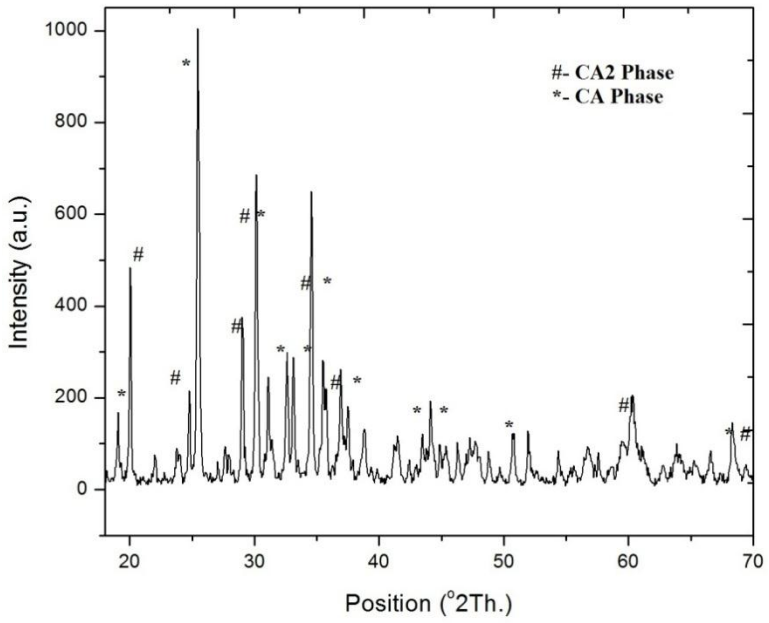


Fig.4.10 XRD analysis of Cement E fired at 1730^oC

The XRD pattern of Group-F cements are shown in the Figure- 4.11 & 4.12. It is observed that Group-F cements contain CA & CA_2 phases only. The major phase present in F-Type cement fired at 1430^oC is CA which accounts 60% (according to semi-quantitative analysis) and CA_2 content is 40%. The CA phase content decreases to 19% when the cement was fired at 1470^oC and content of CA_2 phase increased to 81%. In this batch the alumina content is 72% that is similar to Batch-D but the difference is that here 5% of this calcined alumina is replaced by reactive alumina which is a better variety of alumina. Since the reactivity of this alumina is higher so the CA_2 phase quantity is expected to be higher and that was found here.

Fig.4.11 XRD analysis of Cement F fired at 1430^oC



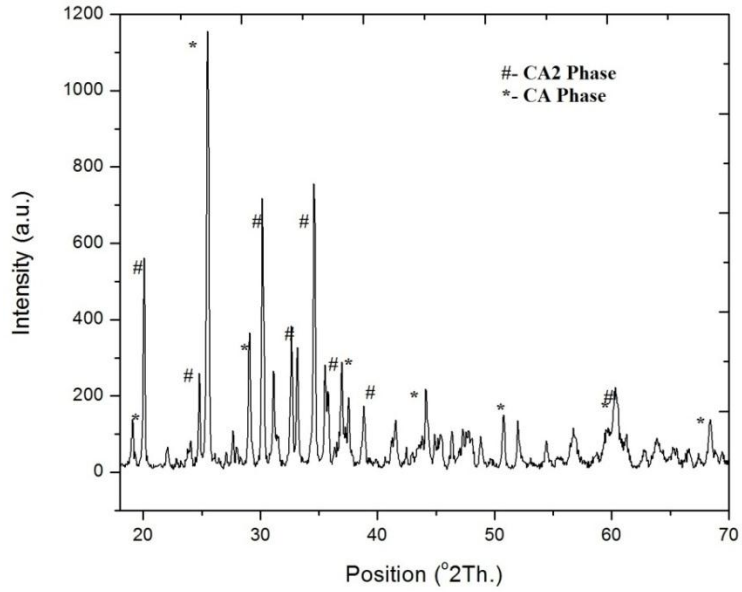


Fig.4.12 XRD analysis of Cement F fired at 1470^oC

Table 4.2 Percentages of Different Phases in All Self-Prepared Cements

Types of Cement	Percent of Different Phases		
	CA	CA_2	CA_6
A/1430	72	28	--
A/1470	59	41	--
B/1430	55	45	--
B/1470	41	59	--
C/1430	16	71	12
C/1470	12	71	16
D/1430	74	26	--
D/1470	66	34	--
E/1430	71	29	--
E/1470	65	35	--
F/1430	60	40	-
F/1470	19	81	--

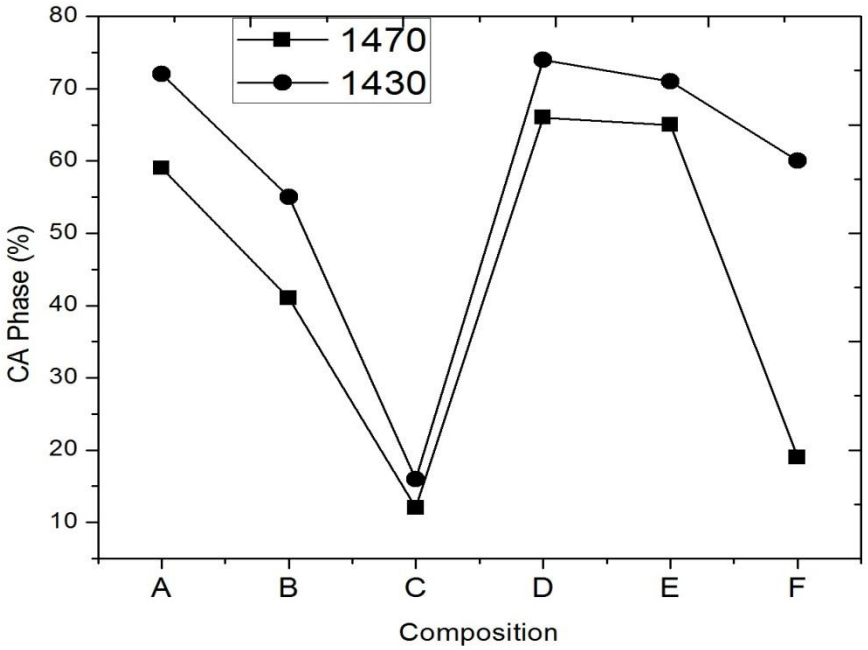


Fig. 4.13 Variation in CA Phase for Different Compositions & Firing Temperatures

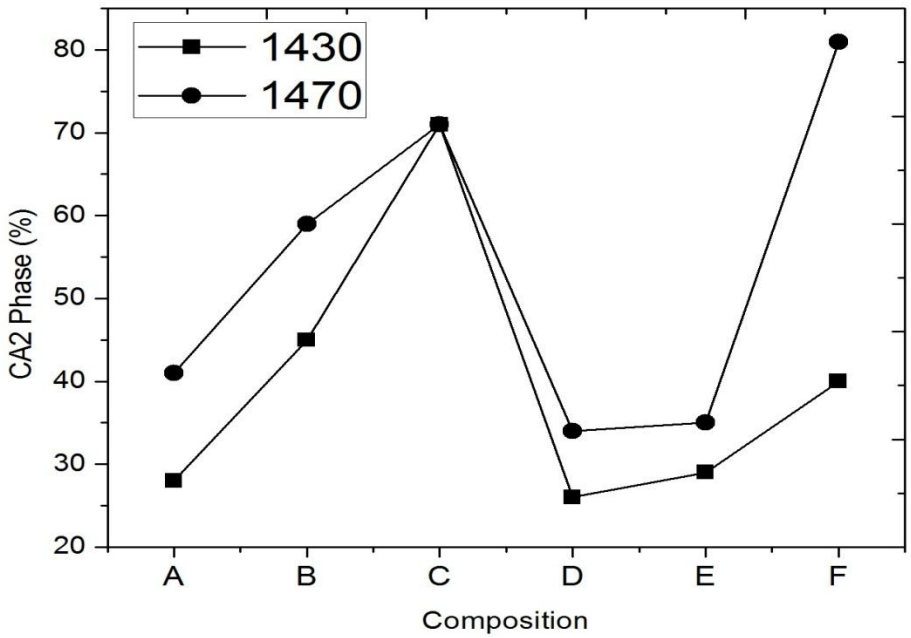


Fig. 4.14 Variation in CA_2 Phase for Different Compositions & Firing Temperatures

Fig. 4.13 shows variation in CA phase with varying composition, for two firing temperature. As the Al_2O_3 content is increasing in the composition A to C the CA phase formation decreases and CA2 phase increases since Al_2O_3 content is increasing so the more Al_2O_3 is present so alumina rich phase forms more. When the Al_2O_3 content is fixed to 72% but 5% of that was replaced by WFA and reactive alumina the amount of CA phase is decreases differently. The WFA containing composition showed little decrement in CA phase content, whereas in reactive alumina containing composition the CA phase decrement is very high. Same for low temperature fired composition has higher amount of CA always. But for higher temperature fired cement has always less amount of CA phase and for 1430^oC compositions showed always higher amount of CA phase for any batch.

Fig. 4.14 shows variation in CA_2 phase with varying composition, for two firing temperature. With the increasing Al_2O_3 content the amount of CA_2 phase increases since compatible for the formation of alumina rich phases. When Al_2O_3 content is fixed to 72% and it is replaced the amount of CA_2 increases. In the case of reactive alumina containing composition the CA_2 phase increases largely than the WFA containing batch. Since reactive alumina is more reactive than WFA, so the reaction proceeds to completion easily and more amount of CA_2 phase formed. For higher temperature fired CA_2 phase is always higher and CA_2 phase is always less than in 1430^oC fired.

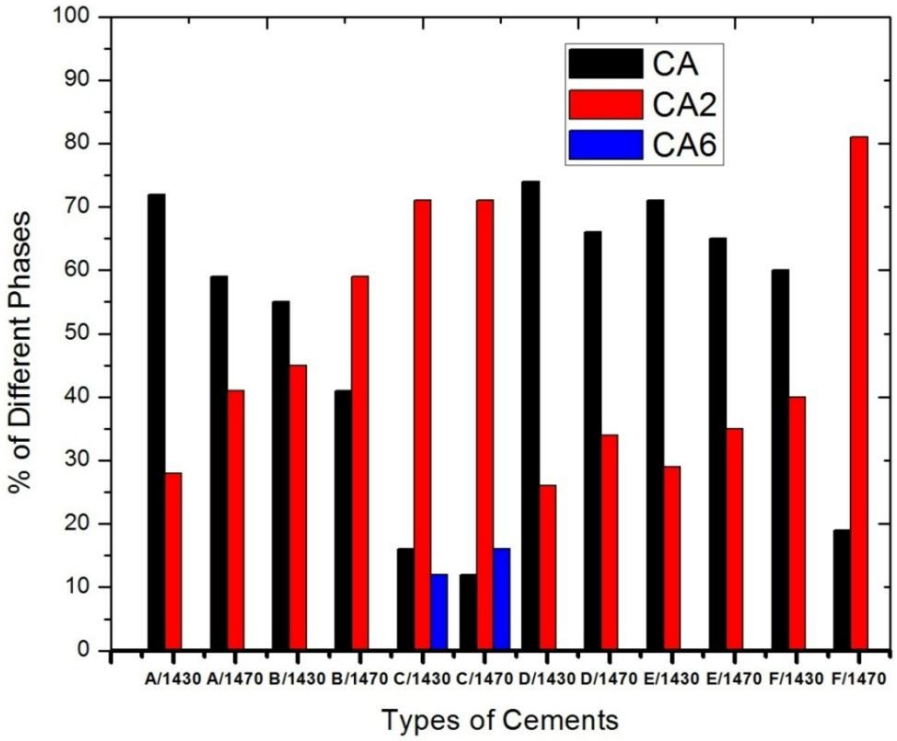


Fig. 4.15 Different Phases in Different Types of Cement

4.2 Characterization of castable group D

4.2.1 Chemical Analysis

The typical chemical analysis result of castables composition provided by the industry is shown in Table 4.3. In industrial practice only alumina, iron oxide, titanium oxide and lime has been tested for castable sample.

Table 4.3 Chemical Composition of Castable Group D

Chemical Component wt%	Castables Group D	
	D/1430	D/1470
SiO_2	26.24	28.01
CaO	0.55	0.74
Fe_2O_3	0.78	0.80
Al_2O_3	61.65	61.65
K_2O	0.21	0.11
Na_2O	0.11	0.09

4.2.2 Mechanical Properties

The result of different mechanical properties like bulk density, cold crushing strength (CCS) & cold modulus of rupture (CMOR) of castable group-D is summarized in Table 4.4. The schematic diagrams of variation of CCS and CMOR with temperature are given in Fig 4.2.

Table 4.4. Mechanical Properties of Castable Group D

Properties	Temperature Detail	Castable Group D	
		D/1430	D/1470
Bulk Density (g/cc)	110^oC/24hr	2.80	2.81
CCS (kg /cm^2) at	110^oC/24hr	1033	727
	800^oC/2hr	765	995
	1400^oC/2hr	982	1084
	1600^oC/2hr	893	816
MOR (kg /cm^2) at	110^oC/24hr	87	105
	800^oC/2hr	56	75
	1400^oC/2hr	87	81
	1600^oC/2hr	93	87

Fig. 4.16 Variation in CCS for Castable Group D

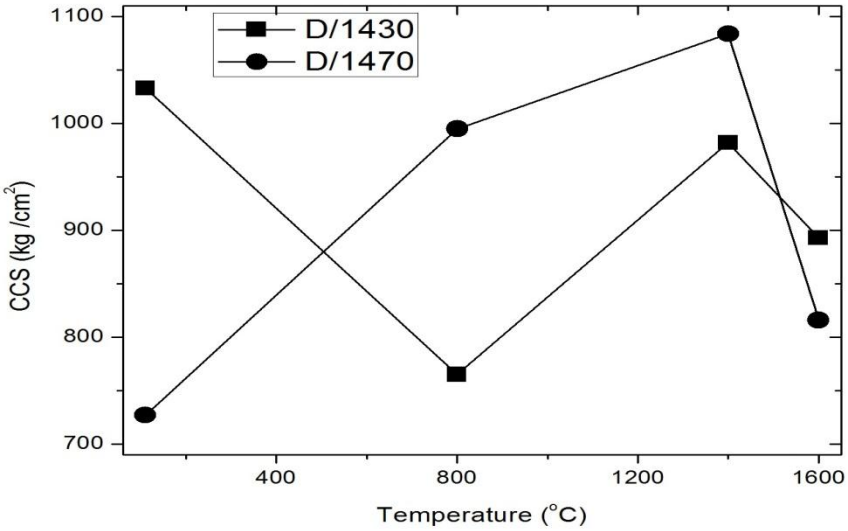
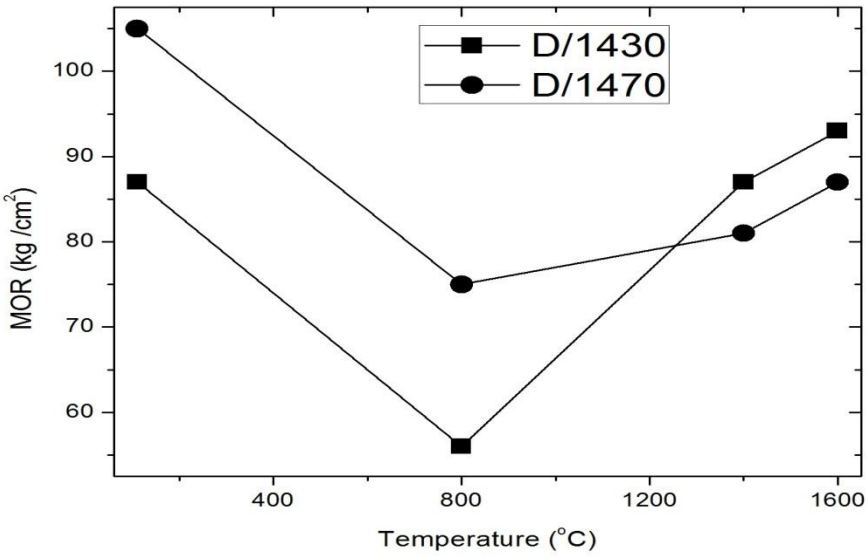


Fig. 4.17 Variation in CMOR for Castable Group D



The CCS of the castable made by using D/1430 type cement is highest at 110^{o}C after 24hr. the reason behind this may be due to the presence of very high percentage of CA phase in the this cement. D/1430 cement contains about ~74% CA. CA phase is responsible for early high strengths in castables.[9] At 800^{o}C the CCS decreases largely. This may be due to the dehydration of the hydrated phases. At this stage hydrogen bonding breaks and leads to strength deterioration. After that again CCS increases at 1400^{o}C but still it is lower than strength at 110^{o}C. This increase in strength is may be due to sintering of castable. The transformation of andalusite aggregate to mullite occurs around 1350-1500^{o}C.simulteniously

mullite formation from alumina, silica bond phases strengthen the castable. The formation of this ceramic bonding is responsible for this strength rise. But after firing at 1600^{o}C the strength falls. This fall in strength may be due to the formation of glassy phase. When andalusite is converted to mullite then the glassy silica phase is expelled out from the andalusite grains. This glassy silica phase and the micro silica both are very reactive phase. But part of the alumina present in the aggregate may remain unreactive which hamper the further mullitisation process. If mullite is not formed then the silica may form liquid phase decreasing the strength of the castable.

D/1470 cement contains lesser amount of CA phase. From the figure it is clear that CCS is very less at 110^{o}C for the castable made by using this batch of cement. The reason behind this may be the lesser amount of CA or higher amount of CA_2 phase present in it. But after that the strength rises up to 1400^{o}C. Rise in strength here may be due to the fact that the major phase present here is CA_2 which shows lesser hydraulic behavior hence gives low strength at110^{o}C. As the temperature increases the dehydration of the hydrated phases is less prominent whereas ceramic bond formation initiated at higher temperature so there is an increasing trend in CCS values. The reason behind the fall in strength in the last stage is same as in the earlier case.

CMOR was also studied. CMOR is following the CCS trend in both types of cement. First it shows high flexural strength then a dip at 800^{o}C and again rises at higher temperatures. The fall in flexural strength may be in response to dehydration of hydrated phases. After that strength rises due to sintering & formation of ceramic bonding.

4.4 Characterization of castable group E

4.4.1 Chemical Analysis

The typical chemical analysis result of castables composition provided by the industry is shown in Table 4.5. In industrial practice only alumina, iron oxide, titanium oxide and lime has been tested for castable sample.

Chemical Component wt%	Castables Group E	
	E/1430	E/1470
SiO_2	27.53	28.05
CaO	0.93	0.74
Fe_2O_3	0.86	0.78
Al_2O_3	61.80	62.17
K_2O	0.17	0.19
Na_2O	0.15	0.20

4.4.2 Mechanical Properties

The result of different mechanical properties like bulk density, cold crushing strength (CCS) & cold modulus of rupture (CMOR) of castable group-E is summarized in Table 4.6. The schematic diagrams of variation of CCS and CMOR with temperature are given in Fig

Properties	Temperature Detail	Castable Group E	
		E/1430	E/1470
Bulk Density (g/cc)	110^oC/24hr	2.77	2.78
CCS (kg /cm^2) at	110^oC/24hr	758	510
	800^oC/2hr	829	1007
	1400^oC/2hr	829	816
	1600^oC/2hr	912	969
MOR (kg /cm^2) at	110^oC/24hr	84	81
	800^oC/2hr	68	62
	1400^oC/2hr	75	68
	1600^oC/2hr	62	93

Fig. 4.18 Variation in CCS for Castable Group E

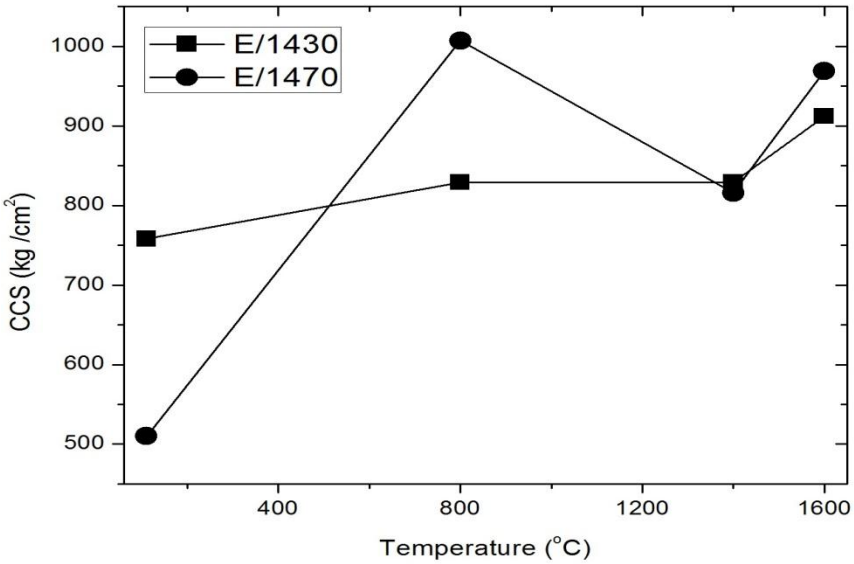
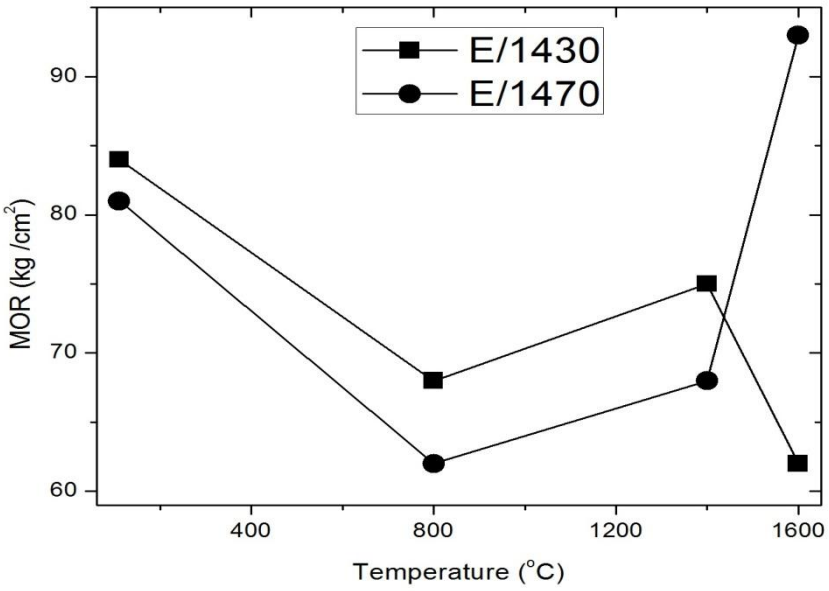


Fig. 4.19 Variation in CMOR for Castable Group E



The castable using E/1430 type cement shows good strength or CCS at 110^{o}C. This may be due to the presence higher amount of CA phase. Higher CA phase more reactive to hydration & better hydration bonding so good strength. The strength remains somewhat constant or same of fired sample at 800^{o}C. The strength then increases as the temperature is rises. The strength reaches its maximum. The reason behind this may be the pore removal, densification & sintering. The ceramic bonding takes place here. CCS of the castable using E/1470 cement at 110^{o}C temperature is very low. This may be due to the higher percentage of CA_2 phase

presence. CA_2 shows lower hydraulic behavior, so lesser hydraulic bonding formation take place hence less strength at 110^oC. Then the strength rises drastically to a maximum. This behavior may be due to the lower amounts of casting water and having a good rheological property. Strength then falls little and then again rises. The strength fall at 1400^oC may be due to the formation of little liquid phase. After that rise in strength of the castable may be due to the densification, sintering and ceramic bond formation.

CMOR of the castables using E/1430 cement is higher at lower temperatures. This may be due to the higher content of CA phase. Higher CA content higher hydraulic bonding formation so higher will be the strength. At 1600^oC, the flexural strength falls. Reason is similar as in case of batch D castables. CMOR of the castable using E/1470 type cement at 110^oC temperature is lower than that of E/1430 type cement; this may be because it contains more amount of CA_2 phase (poor hydraulic comparative to CA phase). In the region between 800-1100^oC, cement bonding phases & relics of cement phases recrystallize first to $C_{12}A_7$ then CA & from 950^oC CA_2 phase starts to form. Flexural strength then increases with the increasing temperature. This rise in strength may be due to the pore removal, sintering & formation of mullite bonding phase in the castables.

4.5 Characterization of castable group F

4.5.1 Chemical Analysis

The typical chemical analysis result of castables composition provided by the industry is shown in Table 4.7. In industrial practice only alumina, iron oxide, titanium oxide and lime has been tested for castable sample.

Chemical Component wt%	Castables Group F	
	F/1430	F/1470
SiO_2	28.17	28.55
CaO	0.74	0.55
Fe_2O_3	0.76	0.86
Al_2O_3	61.56	61.65
K_2O	0.18	0.22
Na_2O	0.14	0.18

4.5.2 Mechanical Properties

The result of different mechanical properties like bulk density, cold crushing strength (CCS) & cold modulus of rupture (CMOR) of castable group-F is summarized in Table 4.8. The schematic diagrams of variation of CCS and CMOR with temperature are given in Fig

Properties	**Temperature Detail**	**Castable Group F**	
		F/1430	**F/1470**
Bulk Density (g/cc)	110^oC/24hr	2.79	2.73
CCS (kg /cm^2) at	110^oC/24hr	867	459
	800^oC/2hr	701	1109
	1400^oC/2hr	765	893
	1600^oC/2hr	1020	969
MOR (kg /cm^2) at	110^oC/24hr	84	65
	800^oC/2hr	62	50
	1400^oC/2hr	112	81
	1600^oC/2hr	118	62

Fig. 4.20 Variation in CCS for Castable Group F

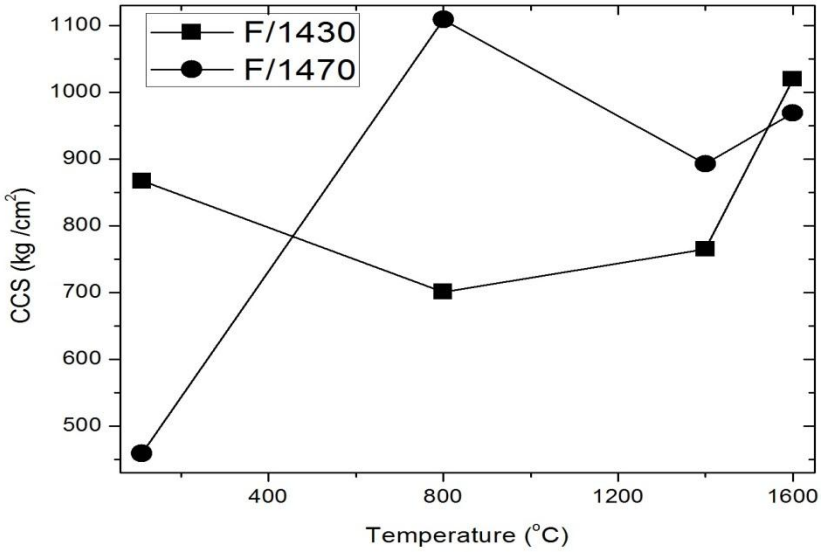
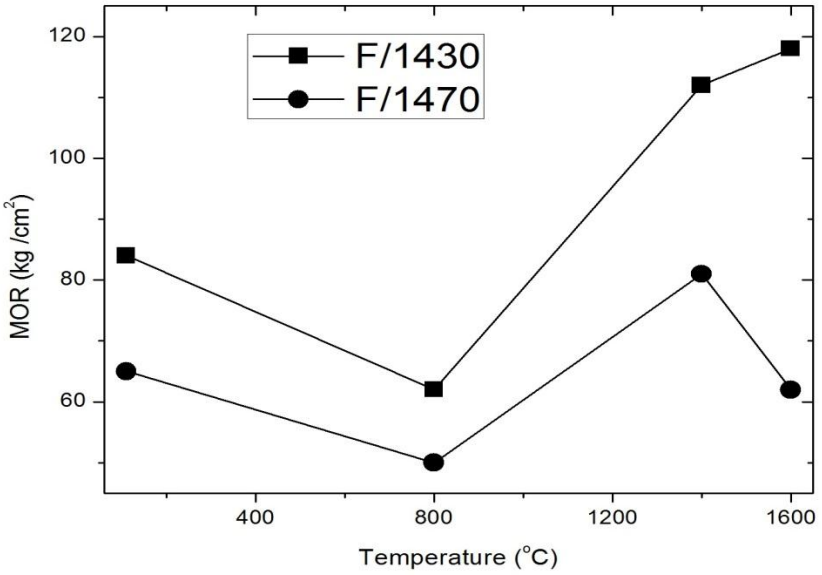


Fig. 4.21 Variation in CMOR for Castable Group F

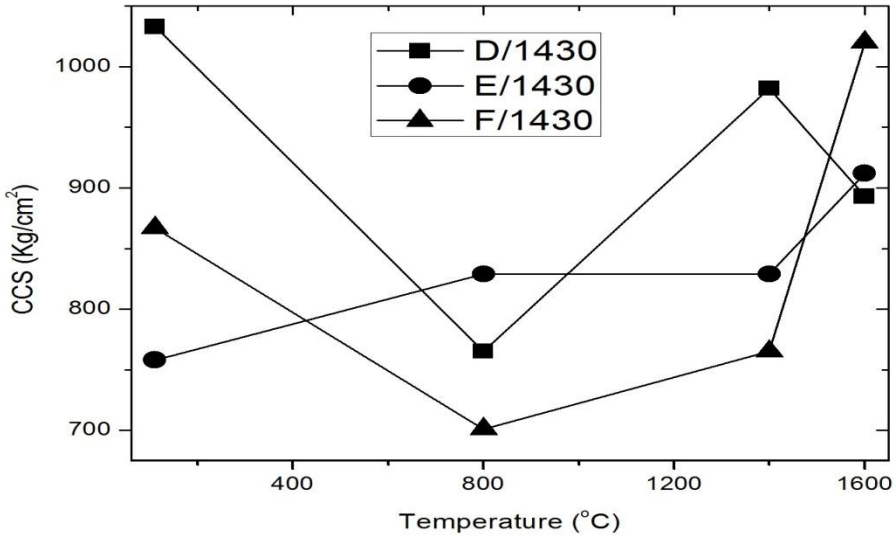


CCS of the castable using F/1430 cement at 110^{o}C temperature is much higher than that of using F/1470 cement. As the F/1430 cement contains higher amount of CA phase. This is responsible for the hydraulic bonding. So the higher CA phase content higher will be bonding & higher will be strength. This follows decrease in strength at 800^{o}C. This may be due to the dehydration or breaking of those hydrated bonds. After that strength increases and reached its maximum. The increase in strength may be due to sintering of castable. Ceramic bond forms and this leads to increase in strength. The strength of castable using F/1470 cement is very

lesser at 110^{o}C temperature. This may be due to presence of higher percentage of CA_2 phase. Here CA phase content is very less, so less hydraulic active phase. So due to absence of sufficient hydraulic phase in the cement the strength is much lower. Then the strength rises drastically to a maximum. This behavior may be due to the formation of ceramic bond in the castable. Strength then falls little and then again rises. The strength fall at 1400^{o}C may be due to the formation of little liquid phase. After that rise in strength of the castable may be due to the densification, sintering and ceramic bond formation. CMOR of the castable using F/1470 cement is very less than the other. Low flexural strength is here again may be directly related to the phase present in cement. As this cement contains CA_2 as major phase and this may be the reason behind very low flexural strength of the castable.

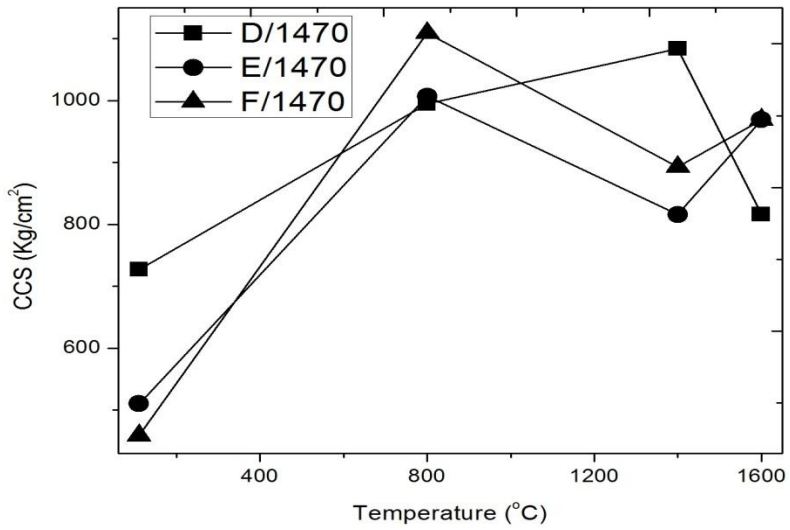
4.6 Comparison of Mechanical Properties:-

Fig 4.22 Variation in CCS of castables prepared by cements fired at 1430°C



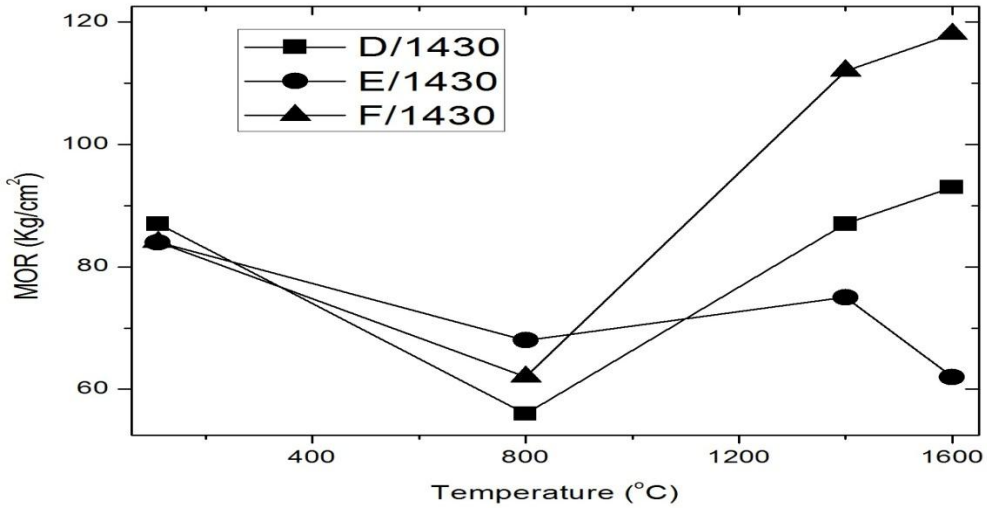
Variation in Cold crushing strength with temperature of castables using all three cements fired at same temperature (1430°C) is shown in figure 4.22. At 110°C, the CCS is maximum for D cement containing castable. This may be due to its large content of CA phase. The strength then decreases due to dehydration of hydraulic bond and then increases due to sintering, densification and ceramic bond formation in all types of castables.

Fig 4.23 Variation in CCS of castables prepared by cements fired at 1470°C



Variation in Cold crushing strength with temperature of castables using all three cements fired at same temperature (1470^{o}C) is shown in figure. At 110^{o}C, the CCS is maximum for D cement containing castable. Again it's true that cement D fired at 1470^{o}C contains highest amount of CA & then decreases. But here cements fired at 1470^{o}C contain lesser amount of CA phase than fired at 1430^{o}C. It's also verified with the strength profiles, strength is lowest for lowest CA phase containing cement. But at higher temperatures the strength of castable is good. At 800^{o}C they showed better strengths. This may be due to that they contains less amount of hydraulic phase CA, so amount of hydrated phases will be less and relics of the cement phases will be higher. Higher strengths at this temperature may be due to the presence of relics of the cement phases and elements of re-crystallized bonding phases in castable. Then strength decreases this may be due to the formation of liquid phase or persisted glassy phase. Sintering and formation of ceramic bonding leads to again rise in strengths at 1600^{o}C.

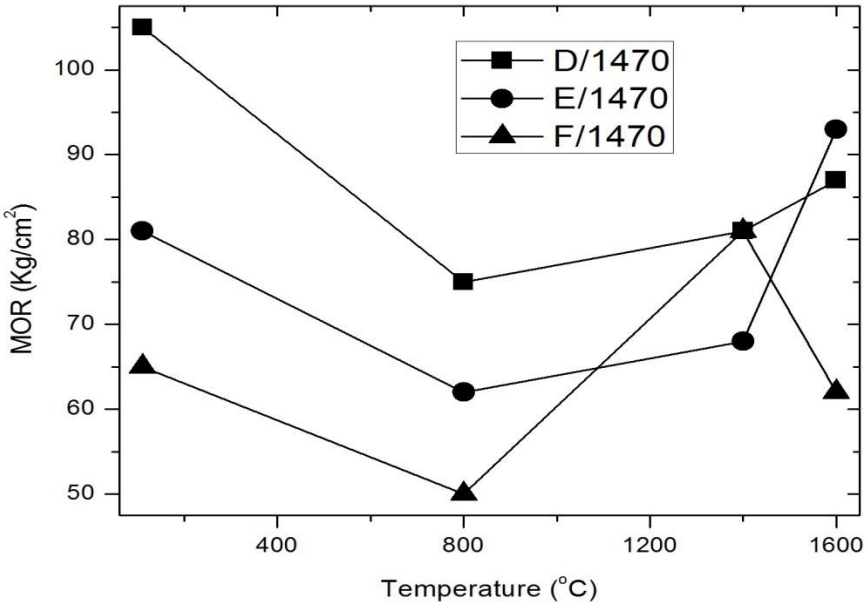
Fig 4.24 Variation in CMOR of castables prepared by cements fired at 1430^{o}C



Initially or at 110^{o}C CMOR is almost similar for all castables, prepared using different cements fired at same temperature (1430^{o}C). At 800oC CMOR drops for all types of cements containing castables and rises with the increasing firing temperature of castable. Strength at 1400 & 1600^{o}C temperature fired castables are higher, the reason may be same as previous (sintering & ceramic bonding). Fall in strength of E sample at 1600^{o}C may be due to liquid or glassy phase formed during sintering.

CaO content in this cement is higher; this may act as fluxing by reacting with impurities like Fe_2O_3 or TiO_2 & producing more liquid phase or it may also form glassy phases like gehlinite (C_2AS) & anorthite (CAS_2) at temperatures more than 1400^oC.

Fig 4.25 Variation in CMOR of castables prepared by cements fired at 1470^oC



Cements fired at 1470^oC lesser amount of CA phase & higher amount of CA_2 phase. For cement F the CA_2 phase content is maximum & its CMOR is lowest at 110^oC. Castable prepared by D cement fired at 1470^oCshowed best CMOR value. This may be again due to presence of higher percent of CA phase in cement. As the firing temperature of castables increases CMOR falls & then again increases. Reasons behind this behavior may be same as discussed earlier (dehydration then sintering & formation of ceramic bond).

Chapter-5

Conclusion

Conclusion:-

In the present work the phase formation in High Alumina Cement were studied by varying manufacturing parameter. Mainly Composition and firing temperature were varied and effect of them was studied in end product. After that those prepared HAC's were utilized in preparation refractory castables and those castables were mechanically characterized. The conclusion of this work can be given as-

- Amount of Al_2O_3 content in the composition affected the amount of calcium aluminate phases formed in the HAC's. Higher alumina content, higher will be amount of alumina rich phases in cement.
- The type of raw material used affected the phase composition of HAC's. With the purity and reactivity of alumina increases more alumina rich phases formed. Reactive alumina produced more amount of CA_2 than by WFA.
- Firing temperature also affected the phase composition; lower firing temperature always produced more CA phase than CA_2 phase and for higher firing temperature, more CA_2 phase formed.
- Castables made from cements having higher CA phase exhibit better strength after 110^oC cured for 24hrs.
- In the dehydration period the strength drop was noted and it was larger in higher CA phase containing cement castables, whereas for higher CA_2 phase containing cement castables the strength drop in this region was not large.
- At higher temperatures, the sintering started and ceramic bond formed and consequently the strength of the castable increases.

Chapter-5

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